

Interactions of trace elements and organic ligands in seawater and implications for quantifying biogeochemical dynamics: A review

Jing Zhang^{a,*}, Gerhard Kattner^b, Boris P. Koch^{b,c}



^a State Key Laboratory of Estuarine and Coastal Research, East China Normal University, 3663 Zhongshan Road North, Shanghai 200062, China

^b Alfred-Wegener-Institut, Helmholtz-Zentrum für Polar- und Meeresforschung, Am Handelshafen 12, D-27570 Bremerhaven, Germany

^c University of Applied Sciences, An der Karlstadt 8, D-27568 Bremerhaven, Germany

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ABSTRACT

Interactions between dissolved trace elements and organic ligands in seawater play an important role in ocean biogeochemistry, ranging from regulating primary production in surface waters to element cycling on basin-wide scale, with strong feedbacks to climate variability. In this study, we review different aspects in the field of marine trace elements and their organic ligands: recent instrumental innovation, factors that affect the fate of trace element complexes at the molecular level, spatial distribution of organic matter – trace element complexes in the ocean, modeling approaches as well as prospect in the scenarios of climate variability. We also assess the critical issues of parameterization in the numerical simulation that incorporate the trace elements – organic ligands interactions. Given the predicted climate changes, we examine the potential of exchange between inorganic and organic complexes for trace elements in different oceanic provinces.

1. Nature of trace elements and organic ligands in seawater

It is commonly known that the trace element (TE) distribution in seawater is affected by redox state and chemical speciation, which not only affect TE availability to biota but also their mobility in biogeochemical cycles of the ocean (Finney, 2003; Morel and Price, 2003; Morel, 2008; Manceau and Matynia, 2010; Tepavitcharova et al., 2011).

About half of the photosynthesis on Earth takes place in aquatic environments (Field et al., 1998), but 30–40% of the marine productivity is limited by the availability of TEs, such as dissolved Fe (cf. Boyd et al., 2007; Boyd and Ellwood, 2010). This reduces the harvesting capacity of solar radiation with significant consequences for CO₂ fixation and eventually for marine ecosystem services such as fisheries. However, not all dissolved TEs in seawater can be used directly by primary producers, because the biological availability depends on their chemical speciation. The term speciation comprises the oxidation/charge of the TEs but also the affiliation to inorganic and organic molecules (ligands). It is well understood that a large fraction of dissolved TEs are bound to ligands in seawater (Hirose, 2006; Mawji et al., 2008; Velasquez et al., 2011; Kim et al., 2015; Noble et al., 2017). Compared to the primary producers in terrestrial ecosystems, for which TEs can be supplied via leaching from rocks and soils, marine phytoplankton faces rather harsh conditions to extract required elements in the euphotic

zone from external sources (e.g. upwelling and atmospheric deposition), especially due to the loss of TEs by organic matter export to the deep ocean. Trace elements delivered by rivers have an important impact on photosynthesis that is constrained in adjacent coastal environments, and this influence is usually reduced towards the open ocean.

Until a few decades ago, the chemical speciation of TEs in seawater was thought to be regulated by their combination with major inorganic anions, such as chloride, sulfate, carbonate and hydroxyl ions, which, as evaluated by thermodynamic models, may account for > 50% of the dissolved concentration for some TEs (Tepavitcharova et al., 2011; Pierrot and Millero, 2017). However, concentrations of dissolved TEs in seawater can be well above the limit of their solubility that is predicted based on chemical thermodynamics of inorganic compounds. For instance, the dissolved Fe concentration in seawater can be as high as a few nM, about two orders of magnitude higher than the so-called “solubility”, which is 0.01 nM for ferric hydroxides at pH = 8.1 and 25 °C (Liu and Millero, 2002). This enhanced solubility (e.g. < 0.4 μm in size by operation) in seawater is promoted by the complexation with organic ligands, which buffers chemical elements against hydrolysis and reduces TE precipitation as inorganic salts containing the major inorganic counter ions such as hydroxides, carbonates, and/or sulfates.

In the ocean, heterotrophic and autotrophic species have developed strategies to produce specific ligands to acquire deficient TEs to fulfill

* Corresponding author at: Visiting scholar at Hanse-Wissenschaftskolleg (HWK), Lehmkuhlenbusch 4, D-27753 Delmenhorst, Germany.
E-mail address: jzhang@sklec.ecnu.edu.cn (J. Zhang).

Table 1

Examples for the large diversity of functional groups (sorted by heteroatom compound classes) that determine the binding of organic ligands with trace elements (not exclusively in seawater). Selected are examples and references of ligand compounds and/or organic molecules. In addition to the type of these functional groups, complex formation strongly depends on the structure of the carbon backbone (conformation/steric effects) and, for marine ligands, on the physico-chemical setting of the seawater matrix (e.g. pH, temperature, and salinity); also, the functional groups can interact and can be linked together by hydrogen bonds in seawater. The role of some of these functional groups in marine organometallic compounds is not well understood and/or identified in seawater. Typical coordination numbers (number of binding sites with the metal atom) range from two to six.

Heteroatom Class	Potential Binding Sites in Organic Ligands			
Nitrogen (e.g. Co, Cu, Fe, and Zn)		Primary amine		Hydroxamate
		Primary amine		Oxime
		Secondary amine		Diamide
		Imine		Imidazole
Examples: Porphyrin-type ligands (chlorophyll, hemes), cobalamine, ferrioxamine, marinobactins, methanobactin, carbonic anhydrase ^{1–6}				
Sulfur (e.g. As, Se, Sn, and Cu)		Thiol		Thioether
		Dithiocarboxylate		Thiocarbonyl
	Examples: Methanobactin, metallothionein ^{7–11}			
Oxygen (e.g. Mn, Pt, Fe, and REEs)		Hydroxyl		Hydrogen-carbonate
		Carboxyl		α-Hydroxy-carboxylate
		Alkoxy		Catechol
	Examples: Catechol dioxygenase, alterobactin ^{1,3,12,13}			
Phosphorus (e.g. Mn, Zn, Cd, and Ba)		Phosphate		Phosphatidyl
		Phosphatidyl		Pyrophosphoric acid
	Examples: Phosphobiotin, phospholipids, adenosine triphosphate ^{14–16}			

their growth requirements. For example, organic ligands that specifically bind to Fe, so-called siderophores, are produced under iron limiting conditions as a deficiency response (Rue and Bruland, 2001; Maldonado et al., 2005; Mawji et al., 2011; Kranzler et al., 2016). Other examples for ligands that are produced to specifically bind to chemical elements in the marine environment include porphyrins that bind to e.g. Mg in chlorophyll, cobalamin (vitamin B₁₂) that contains Co, amino

acids with Se, and various Fe-binding ligands such as ferrichrome, ferrioxamin, or domoic acid (Vraspir and Butler, 2009). Most of these organic ligands form coordination complexes, in which the central atom is a metal cation attached to one or multiple non-covalent binding sites. In this review, we will use the term *organometallic compounds* or *organometallic complexes* and, unless otherwise stated, the term “ligand” will refer to an organic compound. Various functional groups in these

organometallic compounds provide the binding sites for the TEs; these can be amine (as in porphyrin-like ligands), hydroxamate (as in deferoxamine and ferrichrome), hydroxyl, thiol (e.g. as cysteine binding sites in metallothioneins) and carboxyl groups (Morelli and Scarano, 2001; Barbeau, 2006; Butler and Theisen, 2010; Hider and Kong, 2010; Swarr et al., 2016). In Table 1, we provide examples of binding sites in marine organometallics with comparison of inorganic ligands in seawater. It is important to note that these functional groups are not per se binding sites for TEs: the configuration and conformation (changes in the arrangement of a molecule by rotation of bonds) of the organic backbone are critical for the formation of organometallic compounds. Moreover, several and different functional groups are commonly required to bind a metal ion (poly-dentate chelate complexes).

Some of these functional groups, in particular carboxyl groups, also prominently occur in terrestrial and marine dissolved organic matter (DOM; e.g. Benner, 2002; Leenheer et al., 2003), defined as the entirety of organic compounds that pass a filter with a range of mesh sizes of 0.2–0.7 µm. Several studies provided evidence that TE complexation with DOM can be important in regulating the metabolic processes of micro-organisms and phytoplankton, as well as the biogeochemical cycles in the ocean (Rees and Howard, 2003; Morel, 2008; Vraspir and Butler, 2009; Gledhill and Buck, 2012). Marine DOM is a complex mixture of molecules and can be derived from autochthonous and allochthonous sources. The autochthonous DOM can be derived from extracellular metabolic excretion and intracellular autolysis of cells (McIntyre and Gueguen, 2013). It can also be produced along with the heterotrophic decomposition of organic materials and in the progress of grazing. Therefore, the formation of organometallics could either be a result of an evolutionary strategy to acquire TEs (“designer” ligand) or a “random” product of the interaction of TEs with the immense chemical complexity of marine DOM (Benner, 2011).

In this work, we reviewed and synthesized recent progress of studies on the interactions of TEs and organic ligands and focused on the application to understand biogeochemical dynamics of the ocean. In Section 2, we briefly evaluate the innovations of instrumentation that provides possibilities for the determination of organometallics. Section 3 deals with the classification of TEs in the ocean based on their characteristics and relevance to biota, such as biological essential, intermediate and harmful/toxic ions in seawater. Section 4 examines the interrelation of inorganic and organic ligands to form complexes with TEs based on the principles of coordination chemistry. Section 5 summarizes the mode of spatial dimension of organometallics at basin-scale and compares between different measurement techniques. In Section 6, we reviewed recent publications using numerical tools to study TEs in the ocean biogeochemistry and proposed criteria for parameterization in numerical simulations. Section 7 links the study of organometallics with future global change, such as ocean acidification and warming. Finally, in Section 8 we summarized major findings of this work and explored potential “hot topics” of organometallic studies for the future.

2. Challenges of methodology

In oceanography and geochemistry, different approaches of chemical analyses have been elaborated since the late 19th century. For example, the determination of dissolved TE in seawater includes tedious protocols usually starting from the preparation of laboratory wares, sample collection and processing in “clean” condition, and through measurements with state-of-art instrumentation (Table 2).

Historically, inorganic and organic geochemistry in oceanographic studies have evolved in parallel, including the instrumentation. Inorganic geochemistry has been focused on the determination of the chemical composition at elemental and/or isotopic level in seawater; the instrumentation has developed from gravimetric to volumetric measurements, from spectrophotometry at molecular to atomic levels, and electrochemistry up to mass spectrometry. In the meantime, organic geochemistry has evolved from gravimetric and volumetric bulk

measurements in the early 20th century to molecular level gas and liquid chromatography and, later on, their hyphenation with mass spectrometry. Based on the composition and structure of molecules, the organic ligands in seawater can be roughly discriminated as polar/hydrophilic and non-polar/hydrophobic groups, which are believed having different complexing mechanisms and binding capacities with dissolved TEs. This scientific co-evolution resulted in knowledge gaps regarding composition, structure and characterization of organometallic complexes in the ocean, and their role in biogeochemical cycles. Recent innovation of hybrid instrumentation for TEs and organic matter analysis such as ICP-MS and LC-MS, respectively, has shed light on the possibility to quantify the binding ability of TEs in seawaters with organic matter at a molecular level (Lechtenfeld et al., 2011; Boiteau et al., 2013; Garcia-Otero et al., 2013; Mohamed and Gledhill, 2015).

A major challenge in marine biogeochemistry is to develop techniques suitable for clean and quantitative extraction of intact organometallic complexes. This is particularly demanding because of the different requirements of sample materials, the low concentrations of the analytes and the complexity, polydispersity and variable polarity of the organic ligands in the complexes. Solid phase extraction (SPE) efficiency, in addition, depends on sample pH and the polarity of sorbents used (Waska et al., 2015). Using HPLC-ICP-MS coupling and other techniques demonstrated that TEs are selectively bound to specific fractions within the pool of marine DOM (Quigley et al., 2002; Lechtenfeld et al., 2011; Ksionzek et al., 2018). The application of Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS) has also been shown to characterize the combination of TEs (i.e. Cu and Fe) and marine organic ligands (Waska et al., 2015; Walker et al., 2017). In future, any advance of instrumentation with application to ocean biogeochemistry has to take into account two cross-linked factors:

- Separation of TEs in seawater based on their speciation and valence states and measurement of organic ligands that combine with different chemical forms of elements, which provides information relevant to the metabolic roles of TEs in the food-web. The pay-off is that information on organic molecules can be biased because of the elevated organic carbon to TE ratio (i.e. stoichiometry) in seawater. To get sufficient amounts of TE for speciation and even isotope composition analysis, the separation and pre-concentration columns can be over-saturated with respect to organic ligands, and hence the characterizations of organic ligands can be aggravated.
- Separation of organic ligands based on their composition and structure followed by the measurement of the TE and their isotopes combined with different ligands, will shed light on the significance of TE for the oceanic carbon cycle. In this case, the selectivity of TE speciation can be poor, because not all organic ligands combine with TEs, and different ligands can have different preferences on certain speciation of TEs. Furthermore, the determination of the total dissolved concentration of TE can still be a challenge.

3. Categories of TEs and their behavior in the ocean

The challenge for the determination of dissolved TE in the ocean is their very low concentration. Some TE have concentrations as low as pmol/kg to fmol/kg of seawater, but they can be very important in regulating metabolic processes, which in turn modify chemical forms, valances and biogeochemical TE pathways (Table 3). Because of the low concentration in seawater, the analysis of dissolved TE is prone to contamination as well as loss during water sample collection and laboratory processing. In general, high quality TE data were only beginning to appear in the literature after the 1970s.

Based on their physiological and auto-ecological effect in cells, TE in seawater can be categorized as biologically essential, intermediate, or harmful and/or toxic. However, a definite classification of chemical elements in the ocean is not practical because certain elements can be

Table 2

Examples of instrumentation that can be adapted to characterize TEs – organic matter interactions in seawater.

Type of instrument	Applications in chemical oceanography	Remarks
Liquid Chromatography and Mass Spectrometry (LC-MS)	Separation and quantification of DOM	Separation of molecules by various detection methods (polarity, mass, UV, fluorescence, etc.)
Fourier Transform Mass Spectrometry (FT-MS)	High mass resolution of DOM based on soft ionization (e.g. ESI) and <i>m/z</i> detection	Elemental molecular data (e.g. C, H, O, and N), powerful in discrimination and resolution but lacks quantification when used in direct infusion mode
Nuclear Magnetic Resonance Spectroscopy (NMR)	Qualification of organic molecules on resonance characteristics in magnetic field	Rich in information of the organic molecular structure, but requires comparatively large sample quantities
Electro-chemistry, such as polarography (e.g. CLE-ACSV)	Qualification of chemical ligands and conditional stability constants by current and/or voltage	Relevant for organic ligands using different detection windows, no composition and structure of DOM
Electro-thermal Atomic Absorption Spectrometry (ET-AAS)	Quantification of TEs by characteristic absorption of radiation usually in UV	Instrument for single element determinations and chemical forms based on the type of sample handling
Inductively Coupled Plasma Mass Spectrometry (ICP-MS)	Quantification of TEs by plasma ionization and <i>m/z</i> separation	Multi-element and isotope determination and chemical forms based on the type of sample handling
Thermal Ionization Mass Spectrometry (TIMS)	Quantification of TEs by electrical ionization and <i>m/z</i> separation	Concentrations and isotopes determination based on sample handling

limiting at low levels and toxic when exceeding a concentration threshold.

TEs enter biological cells through the uptake pathways for essential metals such as Cd, Co, Cu, Fe, Mn, Ni, and Zn. Note that about 30 TEs and metalloids can be classified as biologically essential in the aquatic environment. For example, Cd, Co, and Zn serve as metal centers and structural elements in proteins, and TEs can also act as active centers for enzymes (Morel, 2008). Biological essential elements such as Cd, Co, Fe, Mn, Mo, and Zn, play a key role in enzymatic reactions including photosynthesis and other anabolic or catabolic processes. For instance, the dissolved Fe concentration in seawater is rather low at 0.02–2 nM, and primary productivity and carbon sequestration are limited by Fe in High Nutrient Low Chlorophyll (HNLC) waters of the surface ocean. It has been reported that > 90% of dissolved Fe in seawater can be complexed by organic ligands, which makes the Fe not readily available to some of the photosynthetic cells in surface waters (Vraspir and Butler, 2009; Gledhill and Buck, 2012), owing to change in bioavailability by forming organometallics. Other elements in this group, including Cd, Co, Cu, Ni, and Zn, also have high affinities to marine organic ligands. In general, as reviewed in Zhao et al. (2016), the bioavailability of TEs depends on the properties of the metal and ligand, their respective concentrations, and species-specific physiological characteristics.

The critical role of biologically essential elements is that they are proactive in enzymatic reactions. They can combine with various organic molecules, e.g. within pigments or vitamins (e.g. Heal et al., 2017), and occur at different element to C ratios in the ocean. Although, at the community level, the organic matter stoichiometry for carbon and macro-nutrients (i.e. N, P, and Si) is well defined by the so-called “Redfield ratio”, TE to C ratios can be quite variable at the organism and molecular level. It has been reported that N-fixing prokaryotes (e.g. cyanobacteria) have higher Fe but lower Zn quota relative to phosphorus (and hence C) compared to eukaryotes, presumably owing to the lack of C-rich structural moieties and a low level of Zn-proteins (Brand, 1991; Twining and Baines, 2013). Moreover, at TE replete conditions, photosynthetic species can accumulate and store essential metals in excess in the cell, and thus change their quota to carbon. Since mechanisms of enzyme reactions can be very different for prokaryotes and eukaryotes, organic end-products of these metabolic processes are expected to be different as well, in terms of quota for TEs to carbon.

TEs of the intermediate group, such as As, Se, and Sb etc., are not necessarily indispensable in the metabolism but could be used by cells via passive or proactive mechanisms through isomorphic and other substitutional pathways, when one or several essential nutrients become depleted in seawater (Orem and Stoltz, 2003; Simmons and Wallschläger, 2005). In the past, it has been thought that arsenic could replace phosphorus in photosynthesis in natural waters having extremely low phosphorus levels (i.e. P-limitation); more recent studies

indicate that in low-DIP (i.e. PO_4^{3-}) waters, some organisms inadvertently take up As and detoxify themselves by converting As (V) to As (III), resulting in mono- and di-methyl As (Wurl et al., 2013). However, it is still under discussion whether photosynthetic organisms can use As instead of P in very low-DIP environments and consensus has not yet been reached (cf. Alberts, 2011; Cotner and Hall, 2011; Wolfe-Simon et al., 2011a,b). Phosphorus is the key element of the backbone of DNA and RNA and a component of phospholipids. It is involved in the energy storage processes and protein phosphorylation. Therefore, the interactive relationship of P and As in seawater has to be examined to understand the mechanisms of As transformation in cell physiology. Similarly, sulfur is an important moiety of the proteinogenic amino acids, cysteine and methionine, as well as of several other biomolecules (e.g. poly-peptides). Selenium can be an analogue to sulfur in the metabolism and replace sulfur in certain proteins and amino acids (e.g. Secysteine). Se is a component of the glutathione peroxidase, which helps removing free radicals and hence protects organic cells from oxidative damages (Price and Harrison, 1988; Dumont et al., 2006).

A few other low-concentration elements, such as Hg and Pb, are not biologically required in the metabolism and can be toxic to plant and animal cells (Sparks, 2005). Toxic elements that are not known of any biological importance can be involved in the metabolic processes through replacement of essential elements. This replacement particularly happens, when the growth rate is limited by the poorly available metal so that the toxic metal can enter the cell through transport mechanisms for the essential element. However, micro-organisms can produce extracellular polymers (e.g. proteins, polysaccharides, and nucleic acids) to bind metals to avoid toxicity. The toxic elements and/or extra influx of essential elements can be sequestered as organometallic compounds (e.g. ATPases or phytochelatins) through efflux systems (e.g. Morelli and Scarano, 2001; Jaroslawiecka and Piotrowska-Seget, 2014).

Many toxic elements are released via anthropogenic activities, such as mining and metallurgy, and enter the cells through pathways of transporters analogue to other metals (e.g. isomorphic replacement). However, they can neither form the chemical bonds with metabolic application nor maintain the biological function as required for essential elements. It has been recognized, for example, that Pb is toxic to biological cells because it can result in changes of nucleic acid and protein conformation, inhibition of enzymatic activity and alterations of osmotic balance (cf. Goyer, 1993; Papanikolaou et al., 2005); countermeasures by the organisms include extra- and intracellular precipitation, adsorption by polysaccharides, binding of elements to the cell wall and export through different transporters (Jaroslawiecka and Piotrowska-Seget, 2014). The overall negative effect is that toxic elements cause the distortion of the molecular structure of organic compounds in cells and eventually create dysfunction of enzymes and proteins. The inventory of these toxic elements in the ocean has been

Table 3
Examples of the combination of TE - organic ligands and the involvement of metabolic processes in seawater.

Elements	Surface water concentration	Examples in metabolisms of cell	Complexing organic ligands	Implications for biogeochemistry
Cd	0.05–2 nmol/kg	Cd is involved in carbonic anhydrase, regulating CO ₂		Inorganic carbon acquisition and substitute for Zn, proxy for P limitation in seawater
Co	5–80 pmol/kg	Synthesis of vitamin B ₁₂ adjusting transfer of carbon and hydrogen	Vitamin B ₁₂	Co-limitation with e.g. Fe, Zn, and B ₁₂ in phytoplankton production
Cr	3–8 nmol/kg	Participation in glucose and lipid metabolism		Redox sensitive and change between Cr(III) and Cr(VI)
Cr	0.1–5 nmol/kg	In ascorbate oxidase and plastocyan, can affect electron transport, ascorbic acid, enzymes of Cu include superoxide dismutase, nitrite reductase and cytochrome oxidase etc.	Domoic acid, phytochelatins, siderophores	Limiting at low level in seawater, but turns to be toxic when higher than the threshold
Cr	0.02–2 nmol/kg	In nitrogenase, nitrate reductase and cytochromes, active center of molecules for oxygen and electron transport, component of iron storage protein, ferritin	Siderophores (e.g. ferrioxamine, amphotin), cytochromes, ferritin	Photosynthesis, carbon fixation, and limitation in N-fixation
Fe	1–10 nmol/kg	Enzyme cleaving water molecule in photosynthesis, arginase that hydrolyses amino acids and destroy undesirable superoxide (i.e. superoxide dismutase)	Amino-peptides	Redox sensitive, indicating anoxic situations and scavenging of particle in water column
Mn	0.1–0.2 nmol/kg	Nitrate reductase and nitrogenase, conversion of NO ₃ ⁻ to NH ₄ ⁺ , N-fixation; enzymes with Mo include nitrate reductase and sulfite oxidase etc.	Molybdo-phores and protein derived ligands (amino acids)	Nitrate assimilation, N-fixation with Fe–Mo cofactor
Ni	0.1–2 nmol/kg	Component of superoxide dismutase, dehydrogenase and urease etc., regulates the disproportional reaction of superoxide, hydrolysis of urea		
V	20–40 pmol/kg	Formation of enzyme nitrogenase and haloperoxidase		Nutrient cycle, potentially for N-fixation and fates of volatile species
Zn	0.05–10 nmol/kg	Formation of alkaline phosphatase and carboxypeptidase and important structural role in DNA binding proteins, hydrolyze P esters and peptide bonds, other Zn enzymes include carbonic anhydrase and carboxypeptidase etc.	Metallothione, carboxy peptides etc.	Micro-nutrient and proxy of Si in the ocean
As	10–30 nmol/kg		Methyl- and ethyl- compounds	Co-evolution with P in biological processes, proxy for P limitation and redox transfer between As(II) and As(V)
Se	0.1–1 nmol/kg	Se-containing amino acid and protein in enzymes to detoxify lipid peroxides	Seleno-amino acids, methyl- and ethyl-compounds	Redox sensitive, link to degradation of organic matter, proxy of paleo-oceanography
Pb	20–60 pmol/kg	Change of nucleides and proteins, inhibition of enzyme activity	Siderophores, methyl- and ethyl-compounds	Anthropogenic emission, atmospheric depositions and water mass movement
Hg	0.5–10 pmol/kg	Change of nucleides and proteins, inhibition of enzyme activity	Methyl- and ethyl- compounds	Anthropogenic emission, and index of transfer in food-webs

dramatically increased because of anthropogenic emissions over the last several centuries, via surface runoff (e.g. river) and sub-ground water discharges into the coastal environment and through atmospheric depositions to surface waters of the open ocean (Boyle et al., 2014; Lamborg et al., 2014; Bratkic et al., 2016).

The environmental cycling of TEs in general and their toxic effect in particular is strongly related to the polarity (and therefore binding sites) of the organic ligand they interact with (e.g. Lechtenfeld et al., 2011). Organic matter from marine waters, terrestrial rivers and lakes has been roughly classified as hydrophobic, hydrophilic, as well as transphilic fractions. It has been shown that in rivers (e.g. Seine), samples from upstream are enriched in the hydrophobic fraction (e.g. humic and fulvic materials), accounting for > 60% of DOC, most likely from natural sources, while downstream from the urban areas the hydrophilic fraction (e.g. carboxylic and amino acids) can be more important (Pernet-Coudrier et al., 2011). At pH = 7–8, 50%–70% of organically bound dissolved Pb in the Seine River can be retained in the hydrophilic fraction while the hydrophobic part accounts for 20%–30%, which presumably enhances bioavailability and reduces the affinity to mineral particles (Pernet-Coudrier et al., 2011). It should be noted, however, that organic molecules in aquatic environments (e.g. seawater) can be of amphiphilic nature. Humic and fulvic materials (acids), which are operationally defined by the extraction method may contain both hydrophilic and hydrophobic groups. Although it is often believed that hydrophobic groups (e.g. aliphatic and aromatic groups) cannot be directly bound to metal ions in aquatic environments, they can contribute to the stability of complexes through π -interactions (e.g. double bonds). This might be particularly favorable when organic ligands replace hydroxide and other inorganic ions through reduction in activation energy (Lawrance, 2010). Moreover, amphiphilic siderophores have been shown to be efficient ligands in natural waters (e.g. Boiteau et al., 2016a).

4. Interactions of TEs and organic matter in seawater

Marine organisms can use a number of pathways for the uptake of TEs. Depending on the metabolic mechanism, this assimilation process modifies TE speciation and valences (Fig. 1). Since most dissolved TEs are bound to organic molecules, organically mediated acquisition is a challenging mechanism for organisms to acquire limiting metals in the water column. For the elements with redox valences (e.g. $\text{Fe}_2\text{O}_3\text{-Fe}^{2+}$ and $\text{MnO}_2\text{-Mn}^{2+}$) the uptake pathway of reduced ions in normoxic seawaters can also be critical. Also, the accumulated intracellular

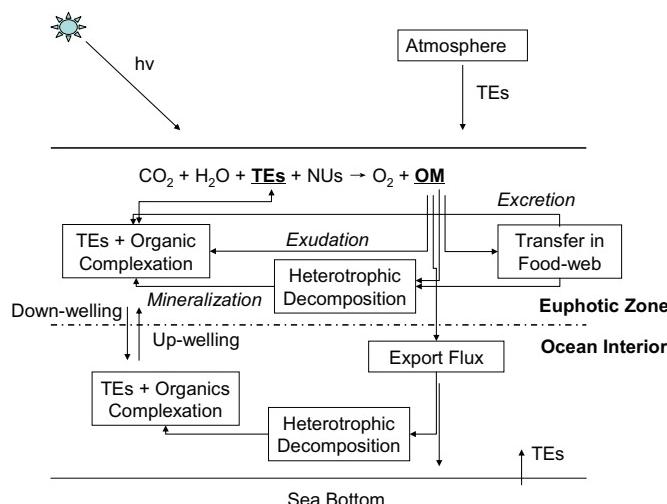


Fig. 1. Trace element – organic ligand interactions and the impact on biogeochemical cycles in the ocean. TEs: Trace elements, NUS: nutrients, OM: organic matter.

concentration of elements can be higher than in the surrounding waters, a result of an active and energy-consuming acquisition of essential TEs. Hence, the bioavailability of TEs in seawater is affected by two factors: the nature of organometallic compounds, and the ability of organisms to utilize these compounds. Dissolved and non-chelated ions can be acquired more easily and hence faster than organically bound metals (Shaked and Lis, 2012). Therefore, the complexation with organic molecules can slow down the biological TE uptake because of a higher energy demand, but at the same time can increase the TE residence time in the water column. However, not all organically bound TEs are available to all organisms. From this point of view, the dissolution enabled by organic ligands and the hindering of cellular uptake are counteracting processes that collectively determine the accessibility of TEs to organisms.

It is known that TEs dissolved in seawater (M) and organic ligands (L) can form various complexes ML_n , with $n \geq 1$. In seawater, coordination numbers of transition metals are usually 4 to 6 but can be up to 12 (Lawrance, 2010). In fact, the single donor (i.e. Lewis base) bond to metal would expose the TE to other ligands, which most likely promotes additional ligands to bind with metals until the coordination number is saturated. Unlike the inorganic ligands that usually form mono-dentate bonds, organic ligands can complex with TEs through a combination of σ - and hydrogen bonds, as well as π -interactions, resulting in poly-dentate (i.e. chelation) molecules with heteroatoms (mainly O, N and S) serving as binding sites with various hard and soft characters (Lawrance, 2010). Higher denticity of a ligand generally increases the stability constant K of organometallics ($K_{\text{chelate}} > K_{\text{mono-dentate}}$). Multi-dentate complex formation results in a favorable entropy change in the reaction, because when a chelate ligand replaces a set of mono-dentate (i.e. inorganic bases) the combination becomes more efficient, that is with a smaller ligand to metal ion molar ratio followed by a higher amount of complex.

To simplify the discussion here, we start by considering the case of a mono-dentate organometallic compound (ML). In seawater, TEs can also be combined with inorganic (X) ligands, such as carbonate, sulfate and chloride, and the reactions can be written as:



where k_1 and k_2 represent the forward and backward reaction rates, respectively. Then the stoichiometric equilibrium constant K_{in}^* can be expressed as:

$$K_{in}^* = \frac{k_1}{k_2} = \frac{[MX]}{[M][X]} \quad (2)$$

Similarly, the complexation of TEs with organic ligands in seawater follows:



$$K_{or}^* = \frac{k_3}{k_4} = \frac{[ML]}{[M][L]} \quad (4)$$

Combining Eqs. (1) and (3) results in:



$$K_{com}^* = \frac{K_{or}^*}{K_{in}^*} = \frac{[ML][X]}{[MX][L]} \quad (6)$$

where K_{com}^* defines the combined stability constant resulting from the release of inorganically bound TEs and subsequent combination with organic ligands. From the principle of mass conservation, the total concentration of dissolved TE (C_M) is:

$$C_M = [M] + [MX] + [ML] \quad (7)$$

Considering a distribution factor (α_i) results in:

$$\alpha_1 = \frac{[M]}{C_M} = \frac{1}{1 + K_{in}^*[X] + K_{or}^*[L]} \quad (8)$$

$$\alpha_2 = \frac{[MX]}{C_M} = \frac{K_{in}^*[X]}{1 + K_{in}^*[X] + K_{or}^*[L]} \quad (9)$$

$$\alpha_3 = \frac{[ML]}{C_M} = \frac{K_{or}^*[L]}{1 + K_{in}^*[X] + K_{or}^*[L]} \quad (10)$$

From Eq. (6), the tendency of inorganic ions being replaced by organic ligands in seawater can be expressed as:

$$\frac{[ML]}{[MX]} = K_{com}^* \times \frac{[L]}{[X]} \quad (11)$$

That is, the ratio of $[ML]$ over $[MX]$ is a function that can be related to the inverse of reactivity of X as well as the inverse of K_{in}^* . In seawater, major inorganic ligands (i.e. Lewis bases) are Cl^- (545.9 mmol/kg), SO_4^{2-} (28.2 mmol/kg), HCO_3^- (1.80 mmol/kg), Br^- (0.84 mmol/kg), CO_3^{2-} (0.25 mmol/kg), B(OH)_4^- (0.11 mmol/kg), and F^- (0.07 mmol/kg). From literature, K_{in}^* ranges from 10^3 to 10^9 and K_{or}^* from 10^8 to 10^{23} , as a consequence of the formation of stable complexes with polydentate ligands (Byrne, 2002; Millero and Pierrot, 2002). In Fig. 2, we investigated effects of K_{in}^* , K_{or}^* , and L on the distribution factor (α_i) of TEs in seawater. If we assume that $[X] = 0.1$ and given the concentration of major ions in seawater mentioned above, Eq. (11) provides a rather conservative estimate on the $[ML]/[MX]$ ratio. Since the organic composition of seawater is poorly known, and hence K_{or}^* for individual organic ligands is not available, we intend to examine the relative importance of K_{in}^* and K_{or}^* on the speciation of a range of TEs in seawater. Here, $K_{in}^* = 10^5$ and $K_{or}^* = 10^{12}$ are used, respectively, for the calculation. These values represent geometric mean values of K_{in}^* for inorganic and K_{or}^* for organic complexes reported in literature (Byrne, 2002; Millero and Pierrot, 2002; Hirose, 2006), shown in Fig. 2a. By increasing the $[L]/[X]$ ratio to $\geq 10^{-6}$, that is $[L] \geq 100 \text{ nM}$, > 90% of dissolved TEs will be bound to organic ligands (L). An upper limit for $[L]$ can be also approximated: at a DOC concentration of $60 \times 10^{-6} \text{ M}$ DOC in surface water, in which each molecule on average consists of 18C atoms (based on FT-ICR-MS analyses; e.g. Ksionzek et al., 2016), the average maximum concentration of $[L]$ is $3 \times 10^3 \text{ nM}$. In the unlikely case that all molecules in DOM contribute to complexation, the maximum $[L]/[X]$ ratio would be 3×10^{-5} . Moreover, in order to have a significant amount of TEs bound to organic ligands (e.g. $\geq 90\%$) with $[L]$ of 10–100 nM in seawater, K_{or}^*/K_{in}^* needs to be $> 10^6$ – 10^7 . Secondly, we used $[X] = 0.1 \text{ M}$, $K_{in}^* = 10^3$ and $[L] = 10 \text{ nM}$ and varied the ratio of K_{or}^*/K_{in}^* from 10^4 to 10^9 and examined the distribution factors (Fig. 2b). The results show that when $K_{or}^*/K_{in}^* \geq 10^8$, > 90% of dissolved TEs can be bound to organic ligands (i.e. “Alpha3” in Fig. 2). In both cases, the fraction of free dissolved TEs, that is $[M]$ in Eqs. (1) and (3), is $< 1\%$, emphasizing the importance of TE complexation in seawater (Fig. 2). Recently, one of the potential siderophores, domoic acid has been studied in the Eastern Atlantic Ocean and was found in concentrations of $\sim 100 \text{ pM}$ in the epipelagic zone (Geuer et al., 2019), which is well below the theoretical value that suggests substantial complexation and about an order of magnitude below the concentration of dissolved Fe (Rijkenberg et al., 2014), indicating that TEs can be combined by other type of organic molecules as well in seawater. Note that organic ligands that combine with TEs may account 1/10 or even less for the total measured DOC concentration (Buck et al., 2018). In the case of domoic acid, the average molar carbon yield in the East Atlantic Ocean was as low as 7.7 ppm (Geuer et al., 2019).

Organic ligands may employ two or more different donors to the targeted metal, and hence chelating rings can be formed (i.e. chelation). In this case, chelates can form much stronger complexes (higher stability constants (K)) than an equivalent pair of simple mono-dentate ligands (e.g. inorganic ions). Another advantage of forming chelating

rings is that the molecules can be amphiphilic (e.g. siderophores), less surface active and hence more soluble and stable against electrostatic and Van der Waals forcings, for example coagulation (Hider and Kong, 2010).

Breaking a metal – ligand bond (e.g. inorganic ions) is almost unavoidably and leads to a follow-up process forming another metal – ligand bond to preserve the coordination number, three-dimensional structure and stability in seawater (Lawrance, 2010). Generally, TEs can form complexes with organic ligands with coordination numbers of 4–6, and the fraction of organic ligands that form organometallics with stepwise coordination numbers, that is ML_i in ML_n ($1 \leq i \leq n$), which can be written as (Harris, 1998; Christian, 2004):

$$ML_i + L = ML_{i+1} \quad (12)$$

with $i = 0, 1, 2, \dots, n-1$, with $i = 0$ and $[ML_0] = [M]$, and the stoichiometric equilibrium constant can be written as:

$$K_{i+1}^* = \frac{[ML_{i+1}]}{[ML_i][L]} \quad (13)$$

and

$$[ML_{i+1}] = \beta_{i+1}[M][L]^{i+1} \quad (14)$$

with

$$\beta_i = K_1^* K_2^* \dots K_i^* \quad (15)$$

From the law of mass conservation, we can have a TE distribution among organometallics as below:

$$C_M^0 = [M] + [ML] + [ML_2] + \dots + [ML_n] = [M] \left(1 + \sum_{j=1}^n (\beta_j [L]^j) \right) \quad (16)$$

Then

$$\alpha_M^0 = \frac{[M]}{C_M^0} = \frac{1}{1 + \sum_{j=1}^n (\beta_j [L]^j)} \quad (17)$$

$$\alpha_{ML_i}^0 = \frac{[ML_i]}{C_M^0} = \frac{\beta_i [L]^i}{1 + \sum_{j=1}^n (\beta_j [L]^j)} \quad (18)$$

Thus, by knowing K_i^* , $[L]$ and $[X]$, one can predict the partitioning of $[ML_i]$ in seawater among inorganic and organic complexes based on the law of thermodynamics. It should be kept in mind that in the above discussions, we did not discriminate between TEs complexes that are composed of different organic ligands (i.e. $L_i \neq L_j$) that can be encountered in seawater; moreover, TEs can also interact with the same ligand molecules but at different coordination numbers.

In a more general case and referring to the Eqs. (1) to (5) as mentioned above, TEs can combine with multiple ligands to form ML_i , that is



and



As for the stepwise replacement reactions in Eqs. (19) to (21), the stepwise stability constant K_i follows the relationship of $K_1 > K_2 > \dots > K_n$. As more and more of one type of ligand is introduced the gain in stability in each step tends to decrease, no matter whether neutral and/or anionic ligands are involved in forming organometallic complexes (Harris, 1998; Christian, 2004; Lawrance, 2010). However, since $K_i \geq 1$, one can have an overall stability constant $\prod K_i > K_1$. The formation of complex with multi-ligands provides advantage of increasing the stability of organic complexes of TE and

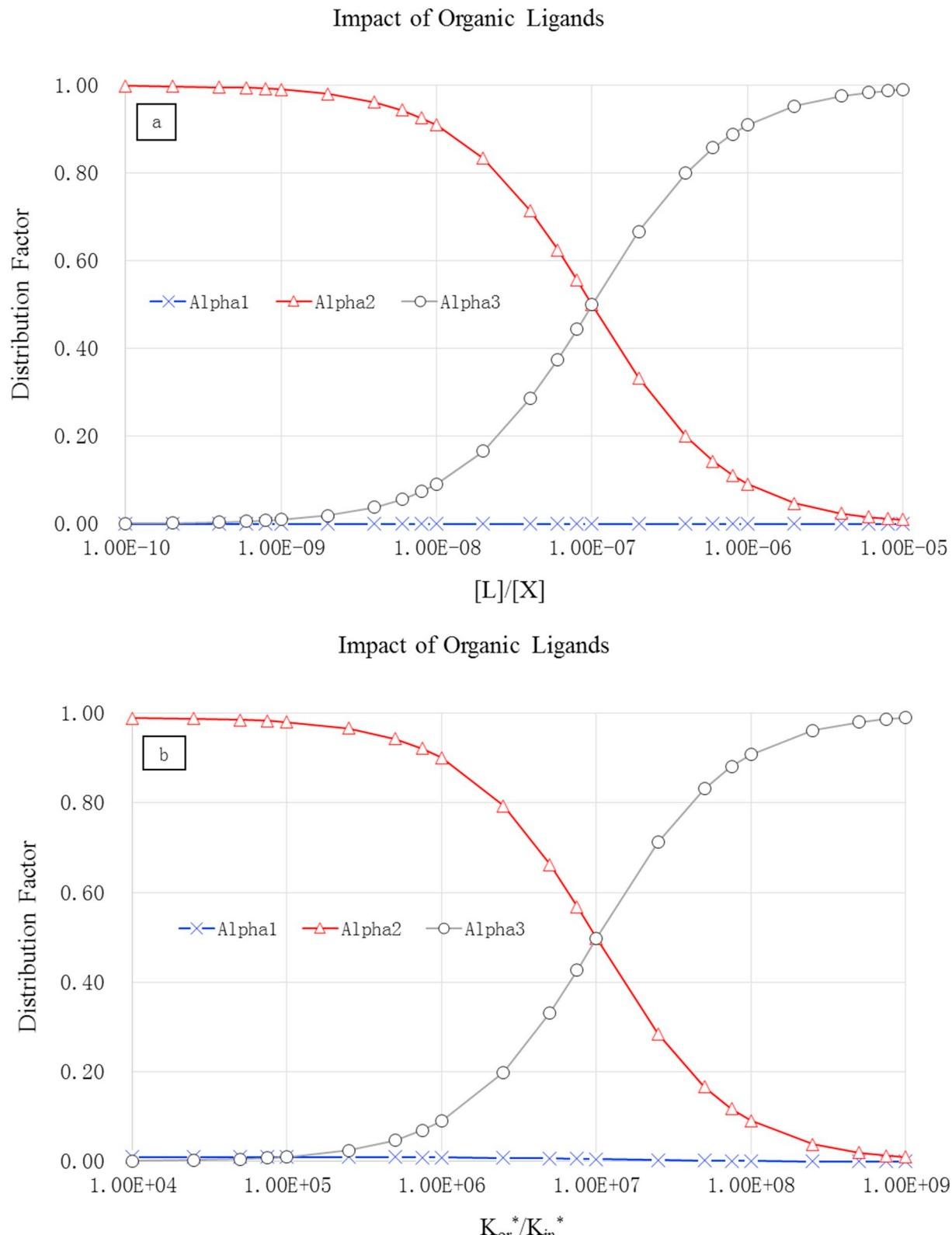


Fig. 2. Variation in the equilibria of inorganic and organic complexes of dissolved TEs in seawater. Distribution factor (%) of free ions ($\text{Alpha1} = [\text{M}]/C_{\text{M}}$), inorganic complexes ($\text{Alpha2} = [\text{MX}]/C_{\text{M}}$) and organic complexes ($\text{Alpha3} = [\text{ML}]/C_{\text{M}}$). In 2a, we used $K_{\text{in}}^* = 10^5$, $K_{\text{or}}^* = 10^{12}$ and $[\text{X}] = 10^{-1} \text{ M}$. In 2b, we used $K_{\text{in}}^* = 10^3$, $[\text{L}] = 10^{-8} \text{ M}$, and $[\text{X}] = 10^{-1} \text{ M}$.

organic pools of TEs with pay-off that there will less ligands available to combine with other elements.

Kinetically, application of thermodynamics in chemical oceanography usually assumes that the system is in steady state and that it is

the end product that counts and is considered (e.g. box model). In this case and as a first order approach, the reverse path of Eq. (5) is usually assumed negligible (e.g. in the application of voltammetry), and hence one can have $k_6 < k_5$, that is the organometallics can be much more

stable than the metal complex with inorganic ligands. This is also the rule in numerical simulations of oceanography in that the “net” products of a given process are considered in parameterization and validation of model outputs. Following Luther III et al. (2015), we consider here that $[ML]$ is the most stable species of M in seawater and the rate expression can be written as:

$$\frac{d}{dt}[ML] = k_3[M][L] \quad (22)$$

$$\frac{d}{dt}[M] = k_2[MX] - k_1[M][X] - k_3[M][L] \quad (23)$$

$$\frac{d}{dt}[L] = k_6[ML][X] - k_5[MX][L] - k_3[M][L] \quad (24)$$

With

$$C_L = [L] + [ML] \quad (25)$$

In the steady state, we have:

$$k_2[MX] - k_1[M][X] - k_3[M][L] = 0 \quad (26)$$

$$k_6[ML][X] - k_5[MX][L] - k_3[M][L] = 0 \quad (27)$$

The solution of Eqs. (26) and (27) is:

$$[M] = \frac{k_2[MX]}{k_1[X] + k_3[L]} \quad (28)$$

$$[L] = \frac{k_6[ML][X]}{k_3[M] + k_5[MX]} \quad (29)$$

Substituting (28) into (22) and taking into account of mass conservation of Eq. (7), one can have:

$$\frac{d}{dt}[ML] = -\frac{d}{dt}[MX] = k_3[L] \frac{k_2[MX]}{k_1[X] + k_3[L]} \quad (30)$$

In the case that TEs in seawater are dominated by organometallics, we can expect to have $[ML] > > [MX]$, and $k_3[L] > > k_1[X]$, then Eq. (30) will be reduced to:

$$\frac{d}{dt}[ML] = -\frac{d}{dt}[MX] = k_2[MX] \quad (31)$$

The integration of Eq. (31) gives

$$[MX] = [MX]_0 \exp(-k_2 t) \quad (32)$$

When $t = t_0$, one has $[MX] = [MX]_0$, which is the same as obtained by Luther III et al. (2015) but the results have much broader application in studying organometallics here. The kinetic reaction rate k_2 in Eq. (32) can be solved as:

$$k_2 = \frac{\ln [MX]_0 - \ln [MX]}{t} \quad (33)$$

Thus if we know the half-life ($t_{1/2}$) of $[MX]$ in seawater, k_2 can be obtained, shown in Fig. 3. In seawater, Millero et al. (2009) and Luther III et al. (2015) indicated that half-lives of MX dissociation in Eq. (5) can be very different, ranging from a few minutes to more than two months. Furthermore, in the case of $k_3[L] > > k_1[X]$, Eq. (26) can be simplified to:

$$k_2 \approx k_3 \frac{[M][L]}{[MX]} = k_3[L] \frac{1}{K_{in}^*[X]} \quad (34)$$

That is, the kinetic rate of decomposition of inorganic complexes is driven by the ease and/or tendency of combination between $[L]$ and $[M]$ in seawater (i.e. k_3), depending on the stability of complex ML over MX . The implication includes that the character and concentration, both in combination, regulate the organic ligands that combine with TEs in seawater.

As an advance for the study on the role of organic ligands, recent research has provided evidence that other TEs such as Cu and Co can be

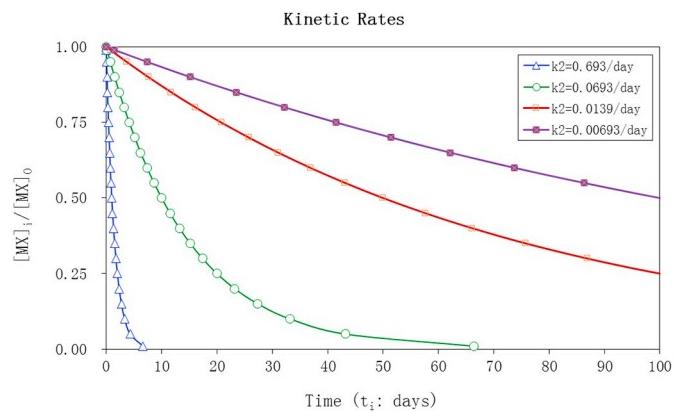


Fig. 3. Kinetic changes in $[MX]$ in seawater (i.e. ratio of $[MX]_i/[MX]_0$) as a function of time (days), showing the stability of inorganic complexes affected by organometallics with a half-life ($t_{1/2}$) of 1 ($k_2 = 0.693/\text{day}$), 10 ($k_2 = 0.0693/\text{day}$), 50 ($k_2 = 0.0139/\text{day}$) and 100 ($k_2 = 0.00693/\text{day}$) days, respectively.

incorporated together with the limiting micro-nutrient Fe because of synergistic functions of multi enzymes (Bundy et al., 2013; Helliwell et al., 2016; Heal et al., 2017). In terms of organic complexation of TEs, one group of ligands in the surface ocean is produced by in situ organic mechanisms (i.e. autochthonous DOM), while other complexing compounds are derived from terrestrial sources (allochthonous DOM) (Bundy et al., 2013; Blazevic et al., 2016). Because the total concentration of dissolved TEs can be lower than the ligand concentrations in seawater, it has been argued that the complexation with organic molecules regulates the cycling of TEs and their biological function in the ocean (Bundy et al., 2013). Indeed, this can have feedback effects on the fate of organic C in the ocean through couplings and fluxes, and it can be expected that the fate of organometallics can affect the pathway and efficiency of the so-called “microbial carbon pump” in a global change scenario. Interactions of TEs and organic ligands can reduce the use of DOM by organisms because the enzymes are highly specific towards the organometallic complex, and there is also evidence that some organisms can access TEs bound to organic molecules in seawater.

Synthesis and exudation/excretion of dissolved organic molecules in the water column are related to the biological activities; hence the composition and diversity of DOM can be linked to the physiology stages in life cycles and metabolic processes of organisms at the species level. It is known that organic ligands (and hence the chelates with TEs) and transporters at the micro-scales of cells can be regulated and accomplished by enzymes at temporal scales of minutes to days, and similar pathways often exist in genomes of either prokaryotic or eukaryotic species, or both. Taking Fe as example, it has been shown that > 200 marine prokaryotes from eight taxa contain genes that can allow using Fe transporters and siderophore biosynthesis in the water column, including 15 major gene groups (Hopkinson and Barbeau, 2012). Similarly, about 30 iron-containing organic compounds and ca. 370 siderophores have been reported in literature (cf. Boiteau et al., 2016a). It was even suggested that trace metal speciation might be an important factor for shaping the gene content of marine heterotrophic bacteria (Hogle et al., 2016). Inorganic Fe(III) in marine environments can be chelated and transported by ATP-binding cassette systems (ABC transporters), including sugars and amino acids among other compounds. Microbial species can transport either Fe(III) or Fe^{2+} across the cytoplasmic membranes (Hopkinson and Barbeau, 2012). In addition to dissolved Fe, some of the gene groups can transport other TEs, such as Mn^{2+} and Zn^{2+} , or they can share or compete for common transport pathways and even multiple pathways of Fe acquisition can exist (Hider and Kong, 2010; Gledhill and Buck, 2012). The organically chelated metals can be released from intracellular pools by grazing or viral lysis, and the transporters at the cell surface can interact with inorganic TEs

for their uptake. Thus, organic complexation can not only modify the speciation and valence of chemical elements but also affect their bioavailability.

Another important factor for TE availability is the competition between groups of organisms and their size-fractions. For instance, Maldonado et al. (2005) found that bacteria within a size range of 0.2–2 μm exhibit the fastest uptake rates of Fe, and the slowest uptake rates are measured for > 20 μm phytoplankton irrespective of abundant organic chelates in seawater.

Colloidal material, in the size spectrum of ca. 10^{-9} m to $0.4 \times 10^{-6}\text{ m}$ by operation also has a high affinity to TEs, especially at a high surface area to volume ratio, but also depends on the chemical composition of the particles (Chuang et al., 2015). With regard to the colloidal organic matter, it has been found that the partition coefficient (LogK_c), the ratio of concentrations between the particulate and dissolved phase, of radionuclides ranges from 4.21 to 6.01 for ^{210}Pb , ^{7}Be , ^{210}Po , ^{234}Th , and ^{233}Pa , and it was recognized that the binding mechanism is controlled by specific biomolecules in marine colloids, e.g. siderophore moieties, rather than lithogenic minerals or authigenic oxides in seawater (Chuang et al., 2015).

The organic moieties of colloidal materials include a variety of binding sites, such as amino, carboxylic, saccharic, and hydroxylic groups (Breitbarth et al., 2010; see also Table 1). Organic sulfur in DOM is a quantitatively important heteroatom in the ocean (Ksionzek et al., 2016) that can potentially provide thiol binding sites. From the theory of Lewis “Hard-Soft-Acids-Bases” (HSAB), hard acids (A-type) such as Fe^{3+} , Cr^{3+} , Ti^{4+} , Th^{4+} , Pa^{5+} , and Be^{2+} prefer to form complexes with O^{2-} , halogen ions (e.g. Cl^- and F^-) and RCOO^- over S and N binding sites, while intermediate and soft acids (B-type) such as Cu^{2+} , Ag^+ , Hg^{2+} , Pt^{2+} , Au^+ , Cd^{2+} , Pd^{2+} , and Pb^{2+} , prefer to bind with CN^- and SCN^- binding sites for S, P and/or N over O and Cl/F binding sites (cf. Chuang et al., 2015). It should be noted that the “hard” and “soft” character for Lewis acids (i.e. TEs) depends also on the charge to radius ratio (z/r) of metal ions, and hence the deformation of the electron clouds when forming chemical bonds. For example, Fe^{3+} is classified as a hard acid whereas Fe^{2+} is an intermediate; Cu^+ is a typical soft acid but Cu^{2+} , which is the major valence state in seawater, is considered as the intermediate (Lawrance, 2010). However, the application of the HSAB theory to understand the complexation of TEs with dissolved organic ligands in seawater has met challenges because a single ligand molecule may contain several charged functional groups but very different binding sites, such as O, S, and N. Also, binding enthalpies depend on the ability to form conformational isomers (structural “flexibility” of the molecule) as well as structural orientations (i.e. left and right rotations). Generally, such isomers are favored for molecules with a higher degree of saturation (sigma bonds). Consequently, it has been observed by Koch et al. (2005) that marine DOM-Na-adducts in electrospray mass spectrometry are favored for compounds with high molecular H/C (higher degree of freedom for rotation) and O/C ratios (higher degree of carboxylation), a trend which likely can be transferred to other non-designer organometallic compounds (Fig. 4).

Similar to C and N, the biological uptake of TEs and the combination with organic matter may cause isotope fractionation. Because the fractionation effect decreases with the increasing atomic mass of elements, it is expected that the isotopic fractionation for most of the TEs (i.e. heavy metals) in seawater is smaller than that for light elements (e.g. H, C, N, and O).

However, there has been increasing evidence of isotopic TE fractionation that can be related to biological processes in aquatic environments. For instance, different isotopic compositions of TEs have been found between abiotic and biotic pools and between low and high trophic groups of the food-web, and microbial regulation of redox reactions can create isotope fractionations, such as for Fe and Cd (Balci et al., 2006; Ripperger et al., 2007; Ellwood et al., 2014). This can induce different isotope compositions in seawater because the measured isotopic difference between two connected trophic levels via food

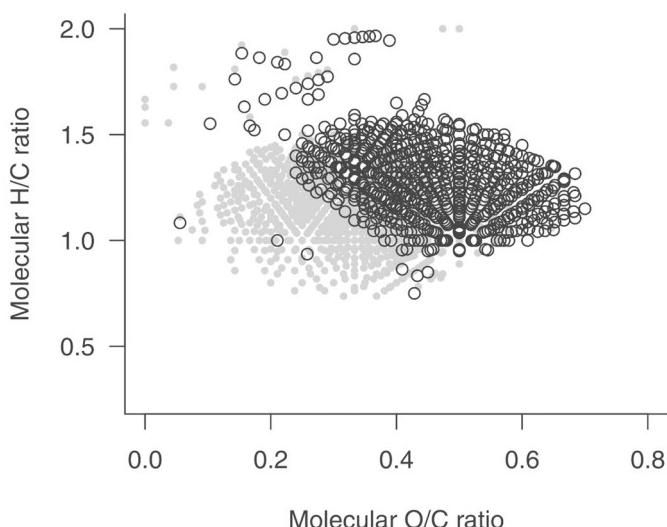


Fig. 4. High-resolution mass spectrometry (positive electrospray ionization mode) of marine dissolved organic matter (modified after Koch et al., 2005): each dot in the plot represents one or several molecular formulas containing C, H, and O. Sodium adduct formation (black circles) occurs at high H/C and O/C ratios. The availability of free electron pairs from oxygen, especially carbonyl functions, assists in the formation of sodium complexes with high binding enthalpies (Armentrout and Rodgers, 2000) and facilitates the formation of intramolecular metallorganic O-Na-O bridges (Kish et al., 2004; Koch et al., 2005).

relationship has an impact on the TEs in seawater (Balci et al., 2006; Percak-Dennett et al., 2011). Further, it has been shown that TE uptake by diatoms can change their isotopic signals (e.g. Zn) in seawater (Gelabert et al., 2006; John et al., 2007). Since phytoplankton selectively use light relative to heavy isotopes in photosynthesis, it can be hypothesized that regenerated TEs along with heterotrophic decomposition of organic materials would generate different isotopic signals in the water column (Cloquet et al., 2008). In the process of biological assimilations (e.g. photosynthesis), a few per mill change in isotopic composition can be depicted using the Rayleigh fractionation model, which is then compared to the observed profiles of TEs (e.g. Cd) (Ripperger et al., 2007). However, biological assimilation and other processes, such as scavenging via adsorption, formation of colloids and redox dynamics can have counteracting effects on the fractionation of the light vs heavy isotope preference. Hence, the profiles of isotope ratios may contradict concentrations and do not show a systematic trend with water depth (Balci et al., 2006; Ilina et al., 2013; John and Conway, 2014).

5. Spatial dimensions of marine organometallic compounds and trace element stoichiometry

In surface waters, solar radiation is believed to have an important role in regulating TE speciation. For example, photo-oxidation can release elements bound to organic material and by that change the TE bioavailability. At shallow water depth, the available TEs may not be fully used by organisms because of the inhibition of photosynthesis by high turbidity as well as damage of cells by UV radiation. However, it is possible that photo-oxidation and heterotrophic degradation of organic matter can be both effective at the same time, and that the released TEs can be incorporated through extracellular enzymatic mechanisms (i.e. recycled production). This, in comparison to the twilight zone beneath, has an advantage in that the change in the chemical speciation and valence of elements can be a net result of the coupling of irradiative and biological mechanisms, e.g. radiation-induced ligand – metal reactions (Cottrell et al., 2014).

Due to the complex composition of marine organic matter,

information on marine organic ligands are available for only a few TEs (mainly derived from titration techniques), such as Fe, Cu, and Ni. The interaction of complex marine DOM and TEs even increases the diversity at the molecular level. Organometallic compounds can be categorized as strong (i.e. L₁) and weak (i.e. L₂ and L₃) ligands, based on the comparison of conditional stability constants (LogK_i). Various analytical methods have been applied to study the conditional stability constants of trace metal – organic matter binding reactions such as ion selective electrode, anodic and cathodic stripping voltammetry, or fluorescence quenching (e.g. Buck et al., 2012; Pizeta et al., 2015). The results show that the conditional stability constants vary over a wide logarithmic range, indicating the diverse nature of the composition and structure of organic ligands in seawater. For instance, the LogK_i of Cu complexes with organic ligands differ by 3 to 9 folds, indicating that very different dissolved organic molecules can be involved (cf. Jacquot et al., 2013; Jacquot and Moffett, 2015). Furthermore, relative to paramagnetic cations (e.g. Cu²⁺) it has been found that diamagnetic metals (e.g. Cd²⁺, Pb²⁺ and Zn²⁺) do not interact strongly with algal-derived DOM (McIntyre and Gueguen, 2013). It has been recognized that there might be artifacts in the determination of conditional stability constants (i.e. K_i) between TEs and organic ligands by titration techniques, because the results depend on the “detection windows” used in voltammetric chemistry (e.g. CLE-ACSV), with various affecting factors, such as type and concentration of added ligands, choice of buffer/pH, hanging mercury electrode drop size, equilibrium time (e.g. reaction rate) and titration data interpretation techniques (Buck et al., 2012; Muller and Batchelli, 2013; Pizeta et al., 2015). Natural organometallics, either too weak or too strong, or both relative to the added ligands can be outside the analytical detection window in titration techniques (Hassler et al., 2011). For instance, it has been found that by using different added organic ligands and different electrode drop sizes, the “detected” natural organic ligands and hence their conditional stability constants can also be slightly different. The observed strong ligands (e.g. L₁) differ between different TEs, such as Fe and Cu (Buck et al., 2012). In the metal titration technique, the stability constant of added organic ligand with target metal ions is known, and the conditional stability constant of metal complexes with natural organic ligands is determined from reactions between added metal and metal-free natural organic ligand, which forms by addition of an artificial strong ligand. However, because the identity of natural ligands is unknown in voltammetric titration, the discriminated ligand types (e.g. L₁ vs L₂) in the water may be operational and not necessarily reflect the nature of organic molecules; nevertheless the technique measures the ability of added organic compounds to release, both thermodynamically and kinetically, the TEs that are originally combined with natural DOM in seawater.

It should be noted again that organic ligands in the marine environment are often in excess relative to concentrations of dissolved TEs (e.g. Fe), even in coastal waters (Louis et al., 2009; Hopwood et al., 2015). If evaluated via stoichiometry between C and TEs, the excess organic ligands can be “seen” from polarography analysis, given that organic molecules can bind with different elements in seawater, depending on the stability of chemical complexes formed and their Gibbs free energy of formation with metals. Using electrochemistry techniques (e.g. polarography), one can distinguish operationally between several major organic ligand groups based on their LogK_i, the strong L₁ and weak L₂ and L₃. It is believed that L₁ includes specific binding molecules (e.g. siderophore for Fe) while L₂ consists of cellular degradation products (Shaked and Lis, 2012). Moreover, both L₁ and L₂ type compounds are subject to photo-degradation in surface waters, which can enhance the pool of dissolved Fe for the uptake by organisms. In natural waters, the high-affinity ligands L₁ can also be of terrestrial origin including humic-type substances with refractory nature, while weaker binding ligands (L₂) are most likely related to the in-situ production (e.g. exudation) and can be more labile (Muller and Batchelli, 2013).

It has been argued that the higher solubility of the reduced form (e.g. Fe²⁺ and Mn²⁺) relative to the oxidized form (e.g. Fe(III)-Fe₂O₃ and Mn(IV)-MnO₂) in the reductive milieu will induce a higher supply of limiting TEs to surface waters, e.g. via upwelling. Various types of organic ligands that complex with TEs to form different molecules have to be considered because decomposition in heterotrophic processes can be slow, and TEs in water masses upwelled to the euphotic zone may not necessarily be in reduced form, however.

Horizontally, there is a strong gradient of DOM from eutrophic coastal water (e.g. estuarine plume and upwelling) to the oligotrophic open ocean (e.g. gyre area), which indicates changes in both concentration and composition of organic ligands. For instance, the strong ligand L₁ for Fe decreases from 15 to 20 nM to 0.4–1.0 nM along a transect from coastal to offshore waters, with LogK_i of 11–12 (Buck et al., 2015, 2018). The concentration of the weak ligand L₂ shows a similar pattern of distribution, but the conditional stability constant (LogK₂) is only 10–11, being comparable between different coastal areas (Buck and Bruland, 2007). In terms of voltammetry measurements, the gradient of DOM is illustrated by the change in concentration of ligands (i.e. ΣL_i) as well as the ratio between strong (L₁) and weak (L₂ and L₃) ligand groups (Buck and Bruland, 2007; Muller and Batchelli, 2013). Using liquid chromatography (LC) coupled to mass spectrometry (Lechtenfeld et al., 2011), the gradients of organic ligand characteristics from coastal to open seawaters are also represented by changes in polarity (i.e. hydrophilic versus hydrophobic character; Boiteau et al., 2016b). It has been noted, however, that ligand molecules in LC spectra with known retention time represent only a small fraction of ΣL_i identified by electrochemical methods, such as voltammetry (Boiteau et al., 2016b). Apparently, the different analytical/detection windows may detect different ligand (L_i) groups for a given trace metal with different proportions between strong (L₁) versus weak (L₂ and L₃) ligands in the sample. Also, for different trace metals, the observed organic ligands (i.e. L_i) can be different in identity, and hence not comparable, even though they can be classified as strong (L₁) and weak (L₂ and L₃) types based on the magnitude of conditional stability constants (i.e. LogK_i). Furthermore, even using the same detection window, the observed organic ligands can have similar L_i characters (e.g. LogK_i) but different identities owing to the lack of knowledge of composition and structure of organic molecules.

Vertically, it has not yet been found that LogK_i for TEs shows systematic trends from surface to sea bottom over a water column of about 5 km (Gledhill and Buck, 2012; Buck et al., 2018). However, the observed LogK_i are variable with depth, which can be attributed to the diversity of organic ligands in different water masses as well as the transfer of organic matter from a labile towards a more refractory character. It has been found that the compound ratio between olefinic and aromatic molecules decreases from the euphotic zone to the sea bottom over a water depth of 5500 m that can be explained by water age and/or type (Hertkorn et al., 2013). Moreover, the concentration of carbohydrates and amino saccharides declines by ca. 75% in the upper 300 m of water column (Benner, 2011). Generally, the concentration of organic ligands and their conditional stability constants show a wider range of variability in surface waters than in the deep ocean. Concentrations of strong (L₁-type) and weak (e.g. L₂-type) organic ligands for Fe can be as high as 5–6 nM in surface waters, and reduce to 1–2 nM at depth of 6000 m (Buck et al., 2015, 2018). With regard to Cu, the organic ligand concentration is 1–5 nM with a conditional stability constant of 12–15 throughout the water column. However, the systematic trend and comparison between different water masses of the deep ocean were not yet elaborated (Jacquot et al., 2013; Jacquot and Moffett, 2015).

The lack of knowledge on the vertical structure of LogK_i maybe in part related to the selection of detection windows: refractory DOM combined with metal ions may not readily be replaced by the added ligands in electrochemistry. Here, it should be emphasized that recalcitrant properties of natural DOM are not directly related to the

stability of organometallic complexes. The chemical reaction depends on the probability of encounters and activation energy that permits the complexation to take place, whereas concentrations of organic ligands in seawater are affected by biological degradation. For example, the strong L₁-type ligands can be specifically produced in surface waters, whereas the weak and non-selective L₂-type ligands are found ubiquitously through the water column. It has been suggested that L₂- and L₃-type ligands can be produced through heterogenous degradation of L₁-type molecules (Buck et al., 2015; Gerringa et al., 2015). The excess organic ligands ($e[L_i]$) in seawater, that is the “saturation” of organic ligand types relative to observed TEs, can be written as:

$$e[L_i] = [L_i] - [M] \quad (35)$$

where $[L_i]$ and $[M]$ represent the concentration of organic ligands and dissolved TEs, respectively, assuming that a 1:1 type of complex is formed (Buck et al., 2015; Gerringa et al., 2015). Similar to the distribution of the total amount of organic ligands, $\Sigma e[L_i]$ in surface waters can be up to 5–6 nM for Fe and decreases to 1–2 nM at depth of 6000 m (Buck et al., 2015, 2018). The positive $e[L_i]$ in the water column usually suggests that organic ligands are higher (i.e. in “excess”) than the amount that is required to bind the dissolved TEs and form organometallics, otherwise $e[L_i]$ becomes negative. It should be noted, however, that $e[L_i]$ can be element specific, e.g. $e[L_i]$ for iron can differ in composition and molecular structure (e.g. binding groups) from other TEs. Alternatively, note that bacterioplankton and eukaryotic phytoplankton have different abilities to access organometallics, such as Fe combined to strong L₁ (e.g. siderophore) and weak L₂ (e.g. monosaccharide) ligands (Hassler et al., 2011). Nevertheless, the observed $e[L_i]$ in literature demonstrates correlations with hydrographic properties (e.g. salinity) and chemical parameters, such as apparent oxygen utilization (AOU) and concentration of dissolved organic carbon (DOC) in the Atlantic and Pacific Oceans and hence the variability in horizontal and vertical scales. For instance, $e[L_i]$ tends to increase with higher DOC and AOU but decreases with an increase in regenerated nutrients (e.g. Si); the excess ligand concentration also increases from south (40°S) to north (60°N) in the deeper part of the water column in the Atlantic Ocean (Buck et al., 2015, 2018; Gerringa et al., 2015).

A reduction of excess ligands relative to dissolved Fe has been found beneath the euphotic zone for two fractions, 1000 kDa to 0.2 μm and < 1000 kDa, corresponding to the regeneration of dissolved Fe and the change in the nature of organic ligands (Thuróczy et al., 2010). Furthermore, a meso-scale Fe addition experiment in the bloom period of Equatorial Pacific surface waters showed a significant increase of Fe-binding ligands (both L₁ and L₂ type) by a factor of four inside the bloom patches relative to the background level (Rue and Bruland, 1997). This suggests that Fe-binding ligands are produced rapidly to combine with the limiting TEs in HNLC regimes.

In summary, results in literature show that separation of organic types (i.e. L_i) is operational and depends on the detection window of analytical methods. Generally, the observed sum of L_i that can complex with TEs represents a small proportion of DOM. DOC/(ΣL_i) can be ≥ 10 and L₁ ≤ (L₂ + L₃) in the water column. Again, it has been found that complexation of TEs (e.g. Fe) illustrates correlations with the sum of organic ligands (ΣL_i) in the ocean. The ratio of strong ligands (i.e. L₁) to a given TE concentration decreases with increasing water depth, and hence a replacement of L₁-type by L₂- and L₃-type ligands for complexation with TEs may take place along the journey from sea surface to bottom (Gerringa et al., 2015). Statistically, the conditional stability constant (LogK_i) tends to decrease with a higher amount of excess ligand concentrations in the water column, and the spatial character (e.g. vertical profiles) of organic ligands differs between Atlantic and Pacific Oceans (Buck et al., 2015 and Buck et al., 2018; Gerringa et al., 2015).

The model proposed to describe the kinetics of TE uptake by microorganisms claims that organometallic complexes have to be broken down at intracellular scales, the element be changed to specific compounds and transported through the cell membrane (Morel et al.,

2008). It has been observed in seawater that the uptake rate of TEs (e.g. Fe) decreases with increasing ligand concentrations, and at high cell concentrations the total uptake rate can be limited by the dissociation of TE complexes via photo-chemical and biological degradation (Morel et al., 2008; Cottrell et al., 2014). In the case of Fe, it has been argued that even under Fe-limited conditions, the unchelated Fe may still sustain a considerable fraction of primary productivity. Concentrations of 0.2–0.3 nM for dissolved Fe can still match the requirement of micro-organisms at a slow and specific growth rate of 0.25–0.35 d⁻¹ (Morel et al., 2008).

Laboratory culture experiments provide evidence that at a dissolved Fe level of ca. 2 nM, the specific growth rate of eukaryotic phytoplankton (e.g. diatoms) in the Southern Ocean can be reduced from 0.5 d⁻¹ to 0.25 d⁻¹ using siderophore complexed Fe (Hider and Kong, 2010; Strzepek et al., 2011). This occurs when the siderophore to dissolved Fe ratio is ≥ 50 and the cell surface normalized uptake rate decreases with decreasing Fe availability. It indicates that the use of organically bound Fe requires more energy through adapting to different uptake mechanisms. For instance, Fe(III) bound to siderophores has to be reduced to Fe²⁺ at an extracellular scale involving enzymatic reactions of e.g. ferric reductase (Strzepek et al., 2011). Moreover, changes in the cellular C concentration with decreasing Fe availability are species-specific, and Fe:C ratios of species from Fe-limited oligotrophic open ocean waters decrease with increasing cell size (Butler and Theisen, 2010; Strzepek et al., 2011), which can be related to the fact that large cells have small surface to volume ratios and hence are affected in the uptake of dissolved metals via surface reactions (Sparks, 2005). Indeed, the observed stoichiometry between TEs and C for natural samples vary over a wide range of molar ratios, depending on a number of conditions and parameters in combination, such as the physiology of cells, community composition, hydrographic properties (e.g. salinity and temperature) and level of nutrients (Twining et al., 2015). Also, it seems that phytoplankton species can use Fe and other TEs bound to various kinds of ligands with different energy trade-offs, regardless of provenance, composition as well as chemical and photo-stability. All these factors affect the bioavailability of Fe as well as other essential TEs and hence their uptake rates, with a mean cellular Fe:C molar ratios of 10⁻⁶ for Southern Ocean phytoplankton species (Strzepek et al., 2011; Velasquez et al., 2016). Other TEs seem to be affected by similar mechanisms when organically complexed forms are used by organisms in seawater. While the concentration of dissolved TEs shows a strong gradient of decrease from coastal waters to the open ocean, the Fe use efficiency was reported to increase towards the ocean interior, from 0.07 × 10⁶ mol C mol Fe⁻¹ d⁻¹ in coastal waters to ca. 0.5 × 10⁶ mol C mol Fe⁻¹ d⁻¹, i.e. a difference by 10 fold (Sunda and Huntsman, 1995; Maldonado and Price, 1996). However, given that organic ligand types (e.g. strong L₁ vs weak L₂ and L₃) differ between coastal and oceanic waters, the observed difference of TEs to C stoichiometry can be a result of changing organometallics, which differ in composition and structure between different samples. Indeed, when there is competition between different TEs for binding sites of excess organic ligands, the metals that can form more stable organometallics, which is favorable in Gibbs free energy, tend to saturate the stronger ligands (e.g. L₁) and leave the weaker ligands (i.e. L₂ and L₃) to co-ordinate with other cations. It has been reported that > 90% of Fe and Cu are complexed with organic ligands, while only 20% to 50% of Ni is organically complexed in seawater (Breitbarth et al., 2010; Jacquot et al., 2013; Gerringa et al., 2015; Jacquot and Moffett, 2015; Boiteau et al., 2016b). From the theory of coordination chemistry, the stability of organic complexes for transition elements in the periodic table of the elements tends to increase from Mn to Cu regardless of ligand, and hence LogK follows the “natural order stabilities” described in the Irving-Williams Series (Lawrance, 2010). Such a difference between observational results (e.g. organometallic Fe and Cu > Ni) and predicted stability by chemical theory sheds lights on that chemical composition of organic ligands can be very different. When they are involved in

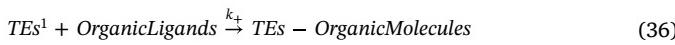
complexation with individual metals (e.g. Fe, Ni and Cu), there is also a possibility that organic ligands are not in excess relative to TEs because ligands can be only a small portion of the DOM.

Finally, most of the biologically essential and intermediate TEs illustrate vertical profiles that are similar to the macro-nutrients in the ocean. TEs taken up during photosynthesis, can escape from the euphotic zone along with the export of organic detritus to the deep ocean, where some of the TEs can be re-mineralized and hence their dissolved concentration increase with depth. Apparently, this does not mimic the rather stable profile of organic ligands (e.g. L₁ vs L₂) through the water column. Along with water depth and/or "ages" of water masses in the ocean, organic molecules that combine TEs, suffer from a change in composition from the "labile" fraction in the euphotic zone to the more "refractory" nature in the deeper parts of water column (Hopkinson Jr and Vallino, 2005; Velasquez et al., 2016). This has an impact on the composition and stability of organometallic compounds, and it can be expected that a fraction of TEs combined with "refractory" organic ligands may not readily be bioavailable even when upwelled to surface mixed waters.

6. Modeling approaches

Ocean models provide a quantitative and dynamic framework that allows better understanding of oceanic cycles of TEs, forecasting and prediction in response of external forcings such as climate change and ocean acidification. Models can also be used to establish testing platforms for designing the experiment and solving unknown parameters, such as estimate on rates. Particularly, modeling approaches can be used to examine the role of TEs in the ocean carbon cycle at basin scales. The key challenge is how interactions between TEs and organic ligands, among other chemical processes, can be incorporated into the biogeochemical module of global oceanic models (e.g. circulation).

Conceptually, the interaction of TEs and organic ligands in seawater can be simplified and written as:



In Eqs. (36) and (37), the superscripts 1 and 2 signify that TEs in water samples can be in different chemical speciation (e.g. valences) and size as well as composition of inorganic ions for the purpose of modeling. The k₊ and k₋ in the Eqs. (36) and (37) represent the rates of reaction. Since we are interested in the "net" products of processes, the reverse pathways are not considered further in the discussion. Eqs. (36) and (37) are different from those of (1) and (3), because in the modeling approach, the parameterization will not consider the individual organic ligands (L_i) but takes into account the net products of reaction, using the concept of functional groups. Model parameterization is usually based on the principle of mass balance, and the net production of CO₂ from decomposition of organometallic compounds is what modelers can link with biogeochemical cycles (e.g. climate related issue).

In the ocean, the organic complexation of the TEs can vary widely in terms of the molecular composition and structure, chemical property (e.g. hydrophobic vs hydrophilic nature), and size spectrum ranging from relatively simple molecules (ca. 10⁻⁹ m) to large organic colloids (i.e. up to 10⁻⁶ m by operation). In Eqs. (36) and (37), k₊ is most likely regulated by the principle of kinetics in chemistry because it depends on the probability of encounter (e.g. collision) of TEs and organic ligands. The reaction can be either first or second order, for reason of simplification a 1:1 ratio between metal and ligand is often assumed in literature (Jiang et al., 2013). The k₋ is specified to characterize the process of decomposition of organometallic complexes in seawater, such as uptake in photosynthesis and/or remineralization by heterotrophic degradation in which organic bound TEs can be released.

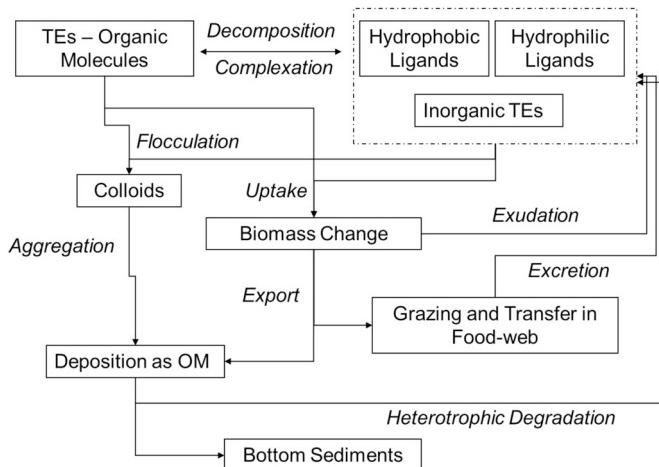


Fig. 5. Conceptual sketch for the parameterization of TEs – organic ligand interactions in seawater for numerical simulations of ocean biogeochemistry.

Organic ligands can be eventually oxidized to CO₂, e.g. via heterotrophic decomposition and photo-chemistry. Again, in the parameterization of modeling approaches, decomposition of organometallics in Eq. (37) is usually considered irreversible, and the steady state is assumed to specify the parameters, such as rate variables.

The new generation of numerical simulations on biogeochemical cycles of the ocean needs to include the function of organometallic modules (e.g. parameterization) that allows examining the interactions between TEs and organic matter at a molecular level (Fig. 5). The dynamic nature of TEs in numerical simulation can be described as:

$$\frac{\partial [TEs]}{\partial t} = AdvectionTerm + DiffusionTerm + ReactionTerm \quad (38)$$

in which "AdvectionTerm" and "DiffusionTerm" are regulated by hydrodynamic processes and can be specified by differential techniques taking into account the gradients of concentration and coefficients for advection and diffusion, respectively. The "ReactionTerm" in Eq. (38) is, however, modeled by the change in element composition through various removal and regeneration mechanisms in the biogeochemical cycle and linked to source versus sink terms of water parcels. For example, to simplify and combine Figs. 1 and 5, the change of "TEs-OrganicMolecules" (TEs-OrgMol) can be written as:

$$\frac{d [TEs - OrgMol]}{dt} = SourceTerms - SinkTerms \quad (39)$$

where "SourceTerms" refers to complexation of TEs with organic ligands, production via e.g. exudation and excretion in the water column, whereas "SinkTerms" takes into account processes such as photo-chemistry, biological uptake and transfer in food-webs, pathways in the microbial loop, and flocculation to generate colloids, which can be depicted through parameterization and quantified by numerical methods after validation using observational data and/or experimental tests.

Currently, the ecosystem modeling approach (e.g. N-P-Z-D model: Nutrients-Phytoplankton-Zooplankton-Detritus) in the oceanographic domain includes the interrelation between the macro-nutrients, the major planktonic functional groups (i.e. photosynthesis and respiration) and the prey – predator relation between phyto and zooplankton at low trophic levels (Fasham, 2003). Although decomposition of organic matter and hence regeneration of nutrients are considered in numerical methods by a module of the microbial loop (Fasham, 2003), the role of TEs in limiting primary productivity and the cycle processes via mineralization are not explored in depth. In the more sophisticated IBM (Individual Biomass Model) approach, the life cycles of key species are considered, and the evolution of the biomass of individuals are

simulated based on hydrodynamics, whereas the importance of TEs in the critical stages of life history is not yet elaborated in detail (Fennel and Neumann, 2004).

Recently, Fiechter et al. (2009) incorporated a Fe-limitation module to N-P-Z-D simulations on the platform of ROMS (Regional Oceanic Modeling System) for the coastal Gulf of Alaska. In the numerical implementation, the Fe uptake in photosynthesis is parameterized using the Michaelis-Menten (M-M) function based on the Fe:C ratio from observations, assuming that all dissolved Fe (i.e. $< 0.4 \mu\text{m}$ in size) is readily available for phytoplankton uptake, which is similar to other ecosystem models but with a Fe limitation component (Fiechter et al., 2009).

Jiang et al. (2013) have used the modeling approach to understand the effect of organic ligands and Fe complexation in regulating primary productivity. In the Southern Ocean around the Antarctic Peninsula, only the 1-D approach has been elaborated, because limited data on dissolved Fe and organic ligands that can be used to constrain parameterization and validation of model outputs in 3-D. In numerical techniques, the N-P-Z-D model is coupled with a Fe module showing the interactions between different pools, such as particulate Fe, colloidal Fe, and bioavailable Fe bound to strong and weak ligands as well as the inorganic Fe. The food-web relationship was simplified to include small phytoplankton and diatoms, micro- and meso-zooplankton (e.g. krill) as well as bacteria (Jiang et al., 2013). The results show that Fe cycling is dominated by the rapid exchange of bio-complexation of inorganic Fe and photo-reduction of organically complexed Fe. Seasonal cycles of dissolved Fe in surface waters revealed a difference of 0.5 nM between winter high and summer low, which is in a similar mode as the seasonality of plant nutrients. The model outputs highlight the indispensability of uptake of ligand-bound Fe in controlling primary productivity in the Antarctic region (Jiang et al., 2013).

In their three-dimensional simulation, Voelker and Tagliabue (2015) considered two main sources of organic Fe-binding ligands: released fragments from degradation of organic macro-molecules by bacteria, and direct production by living organisms, most likely by prokaryotes. The loss processes for organic ligands include bacterial degradation, photo-chemical decomposition, and uptake by phytoplankton, as well as scavenging via colloidal materials. Although the comparison with in situ measurements shows that both models, that is PISCES (Pelagic Interaction Scheme for Carbon and Ecosystem Studies) and RECoM (Regulated Ecosystem Model), can reproduce large scale features of the observed phenomena, such as higher values of ligand in the mesopelagic than abyssal ocean and concentration gradients along the conveyor belt circulation, the models generate unusually high concentrations of dissolved Fe and depletion (i.e. negative excess) of organic ligands. The parameterization is essentially based on the first order and linear relationship among variables whereas synergistic effects such as the competition of TEs for a given type of organic ligands are not incorporated.

At present, the parameterization of TEs in dynamic ecosystem models incorporates but simplifies the processes that drive the biogeochemical fluxes between different function groups at a given niche of the food-web and interactions between different trophic levels of the ecosystem structure. However, the simplification may result in some misunderstandings of biogeochemical dynamics by selecting certain preconceived variables over others, although model behaviors can be tuned to match with the observational data at limited temporal and spatial scales. For instance, in the modeling of Fe-limitation in photosynthesis, the synergic effect of other dissolved TEs, such as Co, Mn and Zn, is not considered and the impact of co-limitation of Fe and macro-nutrients is usually not included in the parameterization, although it has been shown that synergic and co-limitation effects are important for the Fe cycle and interactions between dissolved Fe and metabolic processes in seawater (Mills et al., 2004). It should be also noted that the limiting factor of the so-called “uptake rate” of TEs in photosynthesis is usually parameterized using the Michaelis-Menten type of

equations. A rigorous validation is hampered by very limited observational and meso-scale experimental results. Another question is that using the parameterization based on local measurements and/or laboratory experiments under specific conditions in a global modeling approach (i.e. basin-wide simulation) by extrapolation may generate a biased data set (model output) with an unknown uncertainty, and hence the experimental results themselves need to be tested for a large scale application before being used in parameterization and validation of simulation results (Tagliabue et al., 2017). Currently, most numerical ecosystem simulations consider only a single TE as limiting factor, whereas the synergic effects of TE and major nutrient species as well as co-limiting by several TEs that involves co-functions of different enzymes can be a challenge in the parameterization and validation of numeric techniques in the very near future.

While TEs in seawater may exist in different chemical valences and molecular species, they are lumped and represented by a so-called “total bio-available” concentration in the parameterization. In numerical simulations, the availability of TEs in seawater depends on either their chemical speciation or targeted organisms, or both. Moreover, some of the external forcing factors, such as atmospheric depositions are not well constrained because of the lack of data. Recent studies show that water soluble organic aerosols play a critical role not only in regulating Fe solubility but also in the nature of organic Fe complexes in seawater that affect the availability of dissolved Fe in photosynthetic uptake (Wozniak et al., 2015). It should be also kept in mind that current models of TEs in the ocean are limited to the simulation of Fe. Other TEs, though important in biogeochemistry, are not explored in depth because of lack of knowledge.

It is quite possible that TE complexation results in rather stable organometallics and hence the variation of chemical forms can be slow on time scales that are longer than the uptake by photosynthetic organisms in the water column. Thus, limitation of TEs in primary production depends also on concentration and chemical speciation, as well as kinetics if the supply of available TEs matches the uptake rate of autotrophic species in their anabolism. Moreover, organometallic complexes in the aquatic environment can be of critical importance for the aggregation and decomposition of colloidal materials, for which the dynamic processes are insufficiently constrained by numerical tools, because the molecular composition of colloids is poorly characterized.

Photo-reduction and photo-oxidation in surface waters can be also important for the combination of TEs and organic ligands, particularly for redox metals (e.g. As, Cr, Fe, Mn and Se). The parameterization needs to combine the nature of the radiation spectrum (energy) and photon flux and change with depth, photo-chemistry (e.g. concentration and life time for radicals) as well as their collective effects on the phytoplanktonic community structure. Again, although progress has been made in numeric calculations, observational data are rather limited to validate the model on the impact of photo-chemistry in the real oceanographic domain, e.g. 3-D dimensions at a sub-basin scale.

Since we focused in this review on the understanding of interactions between TEs and organic molecules and their impact on the oceanic biogeochemistry, it should not be forgotten that the coupling of macro-nutrients (N, P, and Si) and TEs can affect the primary producers. As mentioned above, the co-limiting effect of Fe and P (cf. Mills et al., 2004) and of Mn and Fe (Peers and Price, 2004) has been identified, with potential feedbacks on changing the community structure of photosynthetic organisms because of the alternation of enzymatic processes.

In summary, the cycling of dissolved TEs in the euphotic surface waters is regulated by photo-chemistry and complexation with organic molecules. The time scales can be either fast (e.g. diurnal change) or change on seasonal scale (e.g. thermocline), while in the deeper part of water column, the dissolved TE pool is closely coupled to the heterotrophic mineralization by micro-organisms (e.g. prokaryotes), which can be slow because of the limited source/flux of organic matter and the more refractory character of residual organic molecules. There is also

the possibility that TEs released by heterotrophic degradation of organic matter can be complexed again with other but more recalcitrant organic ligands in the water column. Furthermore, the complexation of TEs with organic molecules in seawater affects the structure of the photosynthetic community through changes in uptake dynamics, which in turn modifies the quota of TEs to C in cells as shown in field observations and laboratory cultures (Jiang et al., 2013; Twining and Baines, 2013). Phytoplankton species that can use organically complexed TEs in photosynthesis have great advantages over those using only dissolved inorganic forms, because of difference in bioavailability of TEs to different organisms. This adds another uncertainty in quantifying the biogeochemical cycles in seawater.

It should be also recognized that the progress of modeling approaches on limitation of TEs in seawater is actually retarded by two cross-linked factors. First, the understanding of TEs and organic molecule interactions in seawater is still at its infancy because of challenges in chemical separation and analysis. At this time, the scientific community knows very little about the composition, structure and thermodynamic properties of organometallic compounds in seawater, which requires innovation of methodology to fill the knowledge gap. The second aspect is that the critical role of interactions between TEs and organic ligands in the dynamics of ocean biogeochemistry is missing in current theories; particularly, there is a lack of measurements on “rates” (e.g. kinetic aspects) to testify the mechanism and to quantify the processes, which prevents the validation for simulation results.

Based on the discussions above, we propose following criteria that constrain parameterization and validation of numerical models for organometallic complexes in the ocean:

- Discrimination of complexation with different functional groups at a molecular level, alternatively separation into hydrophilic and hydrophobic classes.
- Link mechanistic understanding of organometallics to the microbial loop, including autotrophic and/or heterotrophic processes, keeping in mind that organometallics in deep waters can be very different from surface ocean.
- Design protocols to quantify the formation rate of organometallic compounds and examine their role in photosynthesis and heterotrophic processes.
- Major biogeochemical pathways affecting organometallics in seawater should be incorporated, such as photo-chemistry and excretion, particularly when recycling of TEs in surface waters is of concern.
- Simulation of dynamics should take into account the wide size spectrum from the true dissolved form to colloidal fractions, including organic macro-molecules and transfer from inorganic complexes to organometallics.
- Examination of different roles of prokaryotic and eukaryotic organisms in regulating organometallics, including cross-links between anabolism and catabolism, because they usually represent different function groups in ecosystem dynamics.
- Comparison of various enzymatic pathways of organometallic complex formation and degradation to better understand the co-limiting nature of TEs and synergistic effects.
- Parameterization should take into account different time scales of dynamics for TEs – organic ligand interactions, from seconds/minutes for fast rates in the microbial loop to weeks/seasons that cover the life history of planktonic/nektonic species.

Nevertheless, “patchy” and “ephemeral” nature can be encountered in process studies of ocean science, such as algal blooms and hypoxic phenomena, riverine plumes and upwelling etc., in coastal area. These phenomena occur in meso-scale and/or even smaller spatial dimensions that affect the fate of organometallic compounds, and hence the behavior of models that should be considered in future development.

7. Lower pH and warmer ocean in the future: implications for trace elements and organic ligands

Given the anthropogenic perturbations on the global scale over the last centuries, the climate change and ocean biogeochemical cycles have become two cross-linked topics but their future remains largely uncertain (Hoffmann et al., 2012). Among various challenges of predicting the impact of climate change, decrease in seawater pH (i.e. “acidification”) and warming are recognized as two important phenomena that affect the sustainability of the ocean ecosystem. In seawater, OH^- , HCO_3^- , B(OH)_4^- and CO_3^{2-} can form strong complexes with divalent and trivalent TEs that are hard acids (A-type) in the HSAB theory. With decreasing pH, OH^- and CO_3^{2-} are expected to decrease in surface waters by about 50% over the next 150–200 years at atmospheric $p\text{CO}_2$ of 500 μatm . The model prediction indicates that concentrations of these two anions are expected to drop by 82% and 77%, respectively, if atmospheric $p\text{CO}_2$ increases up to 2000 μatm (Millero et al., 2009; Gledhill et al., 2015). In Eqs. (1) to (5), the reduction of inorganic ligands [X], such as OH^- and CO_3^{2-} along with the ocean acidification, will induce dissociation of [MX] and release of TEs that are originally combined with [X], which in turn promotes formation of organometallics with different composition. Hence, TEs that form strong complexes with OH^- and CO_3^{2-} will have a higher free ion fraction in a lower pH surface ocean. Moreover, most trace metals become more soluble at lower pH. A lower pH also affects structure and TE binding affinity of organic ligands having acidic functions, such as carboxylic functional groups (Kim et al., 2016), because additional protons compete with the TEs. Marine DOM predominantly contains carboxyl groups, which are suitable binding sites for TEs, and which are strongly affected by a changing pH (Millero et al., 2009; Hoffmann et al., 2012). Both processes in combination control the TE speciation in the future ocean. Moreover, more acidic micro-environments affect the metabolic processes of microbes and their role in the carbon cycle.

Experimental results showed that a lower pH can result in an overall decrease in the side reaction coefficient and an increase in dissolved TEs (e.g. Fe and Cu) in coastal waters (Gledhill et al., 2015). Since terrestrial input is an important source of dissolved TEs to the global ocean, the increase in inorganic TEs will potentially promote the combination with natural organic ligands especially in the coastal ocean. Given that OH^- , B(OH)_4^- and CO_3^{2-} are most sensitive to the change in seawater pH in the future, it can be expected that the TEs in the hard acid class (A-type) are more apt to the impact of a lower pH because they tend to form complexes with hard bases (e.g. OH^- and CO_3^{2-}), while soft acid (B-type) TEs are less affected by a lower pH. The reduction of OH^- and CO_3^{2-} in seawater may correspond to an increase in $[\text{L}]/[\text{X}]$ (Fig. 2). This will modify the partitioning of TEs between inorganic and organic ligands, with a profound impact on the element availability to biota, particularly when the synergistic effects of TEs are of concern.

The details of the impact of global change on the interaction between TEs and organic ligands are not yet clear. The model prediction indicates that warmer, more stratified and acidified surface water will induce lower productivity but drive enhanced photo-chemical and bacterial modifications of organic ligands (Voelker and Tagliabue, 2015). In seawater, photosynthesis and respiration have different correlations with changing temperature, and it can be expected that the ratio between autotrophic and heterotrophic DOM will be altered as well. Because community respiration is more sensitive to temperature increase than photosynthesis, it can be expected that the organic ligands can be altered in a warming ocean (Hoffmann et al., 2012). With changing organic ligand concentrations in the future ocean, TE limitation (e.g. Fe) may be more serious, and the relative importance of these effects needs to be tested using observations and laboratory experiments. Diagnostic models of the future ocean should have the capability of simulating different organic ligand classes (i.e. functional groups) with different reaction rates as a function of temperature, rather than total ligand concentrations alone.

Studying the interaction of TEs and organic ligands has a number of implications for our understanding of chemical oceanography. For instance, understanding interactions between dissolved TEs and organic ligands at molecular level can help discriminating between different chemical mechanisms, and providing information on thermodynamics and kinetics, such as equilibrium constants and reaction rates. Knowledge of reaction kinetics of organometallic compounds will allow to build-up modules of parameterization in process studies; the observational data themselves can be very useful for model validation.

In global change science, knowledge of these interactions will definitely help to improve numerical models at basin scale, contributing to a better understanding of the global C cycle, and improved understanding of transfer and fractionation of chemical materials between different marine trophic levels (Breitbarth et al., 2010). Predictions on the interaction of TEs and organic ligands in scenarios of climate change should be tested with observational data. The major drivers that affect the interaction of TEs and organic ligands include a number of cross-linked key factors that combine reaction rates and environmental conditions, such as temperature, pH, salinity, photo-radiation, and their combinations. It should be noted that the life history of most biological species in the ocean is rather short relative to the slow but consistent rate of lowering pH and continuous warming. Hence using the knowledge obtained from short-term laboratory experiments and/or mesoscale essays to predict the ecosystem response to the climate change can be particularly challenging.

In coastal environments, the amplitude of the daily or seasonal variability of water temperature and pH can be larger than the slow rate of sea level rise and acidification that can be seen at annual scale in temperate climate. This aspect might also bias numerical models of TEs – organic ligand complexation that are based on linear relationships, for example, between pH and biological processes.

8. Perspective and way forward

Compared to inorganic TE complexes with major ions in seawater, interactions of dissolved TEs and organic ligands have a number of biogeochemical functions and merits that should be considered in near future studies:

- Organic ligands can form multi-coordinate complexes with TEs, i.e. ML_n , with n up to six and even higher, resulting in conditional stability constants K_i that can be much higher than for inorganic complexes (Butler and Theisen, 2010). It is therefore important to develop new protocols that allow determination of $[ML_i]$ ($1 \leq i \leq n$), and the partitioning of organometallics with different coordination numbers.
- Some of the organic ligands (e.g. siderophores) have a self-assembled structure, with a hydrophilic peptide head and a long fatty acid tail with up to 20 carbon atoms. This allows coordinating of TEs (e.g. Fe(III)) with the peptide head group and prevents flocculation in seawater (Martinez et al., 2000). The structure of organometallics has a dramatic effect on the thermodynamic stability and kinetic reaction rates, e.g. k_2 vs k_3 .
- Organic ligands are of biological origin and are produced, e.g. by bacteria, to complex TEs to reduce toxicity or stabilize the TEs for uptake (Semeniuk et al., 2015). Chemical characterization of organometallics can thus provide information on the source of organic ligands.
- The same organic ligands can combine with different TEs, which can promote the synergic effect and/or catalyze the uptake of other metals (Whitby and van den Berg, 2015). In seawater, poly-dentate organometallics are likely to have a higher impact on the the biogeochemistry of TEs compared to the mono-dentate complexes (e.g. inorganic compounds).
- TEs bound by organic ligands can also be used by organisms, although the rate of uptake can be slower than for the free ions

because of a higher energy demand. However, uptake of organically bound TEs may become more important in the global change scenario (Kustka et al., 2015), with potential impacts on plankton community structure.

- Since organic ligands are usually in excess relative to TEs in seawater, the complexation can help to stabilize the dissolved TE concentration (i.e. high K^* and L) (Sander et al., 2015). Slow uptake processes, on the other hand, correspond to an increase in residence time of TEs in the water column.
- The observed complexation of organometallics are higher for Fe and Cu than Ni, which needs to be compared with the theoretic prediction in coordination chemistry (e.g. “Irving-Williams Series”) that is based on the complexation with simple organic ligands, such as amino acids (e.g. glycine), oxalate, malonate, and succinate (cf. Lawrence, 2010). In seawater, a given TE can complex with different ligands, and the proportion of organometallics to the total TE concentration is a result of collective contribution of various bindings.

Moreover, organic ligands may have multiple binding sites, containing heteroatoms such as N, O, P and S in a single molecule, allowing selective combinations (σ - and π -bonds) with either hard or soft acid metals; H can form hydrogen-bonds that stabilize the organometallics in seawater. Again, compared to inorganic complexes, organic ligands are highly selective in combining with TEs. For example, siderophores coordinate to Fe(III) rather than to bivalent positive cations, such as Zn^{2+} , Cu^{2+} , Ni^{2+} and Mn^{2+} , because of charge differences in coordination of multitude bound complexes (i.e. charge effect) (Hider and Kong, 2010). Also, Co(III), Cr(III), Al(III) and Fe(III) can be discriminated in forming complexes with siderophores, because their radius differ by 20% and more (i.e. steric effect). Another reason is that when Fe is released from organic complexes (e.g. siderophores), Fe(III) is reduced to Fe^{2+} , whereas a similar mechanism does not exist for Al, Mn as well as for Cr (Hider and Kong, 2010; Luther III et al., 2015).

In summary, for a given TE in seawater, its partitioning (K_{pi}) between major inorganic ions (X_i) and organic ligands (L_i) can be generalized as:

$$K_{pi} = \frac{\sum [ML_i]}{[MX_i]} = \frac{[M] \times \sum_{j=1}^n (\beta_j [L_i]^j)}{[MX_i]} = \frac{1}{K_{in}^* \times [X_i]} \times \sum_{j=1}^n (\beta_j [L_i]^j) \quad (40a)$$

based on Eqs. (2) and (16). In seawater, the concentration of major inorganic ions (X_i) is a function of salinity. Therefore, our knowledge of K_{in}^* is relatively solid and the term $\frac{1}{K_{in}^* \times [X_i]}$ can be considered as constant. Consequently, K_{pi} of TEs changes in different parts of marine environment but can be generally $>> 1$. However, in seawater, there exist many different types of organic molecules, and hence we have $L_i \neq L_j$ for organic ligands. Thus, different organic ligands compete for the complexation with limiting TEs, and the stability of complexes is depicted by the Gibb's free energy of formation. The K_{pi} differs between different organic ligands and varies according to TEs of interest. It should be noted that in Eq. (40a) requirement of the term $\frac{1}{K_{in}^* \times [X_i]}$ being stable is in condition of constant seawater pH, because of variability of K_{in}^* . However, for a given water mass in the ocean, seawater pH is usually in a narrow range. For example, the daily variability of surface seawater is $pH = 8.10 \pm 0.10$ for the open ocean.

Comparably, the competition for TEs between strong (L_1) and weak (L_2) organic ligands in seawater can be evaluated as:

$$\frac{[ML_1]}{[ML_2]} = K_{L_1/L_2}^* \times \frac{[L_1]}{[L_2]} \quad (40b)$$

where $K_{L_1/L_2}^* = \frac{K_{L_1}^*}{K_{L_2}^*}$. Eq. (40b) is similar to (11) but emphasizes the competition of TEs for different organic ligands of varying strength (see also Fig. 2). From Eq. (40b), change in composition of organometallics

depends on the products of the stoichiometric equilibrium constant ($K_{L_i}^*$) and the concentration of ligand (L_i). Thus, in the case of $K_{L_2}^* \times [L_2] \gg K_{L_1}^* \times [L_1]$, weak ligands (e.g. L_2) can also dominate the organometallics and hence the organic fraction of dissolved TEs in seawater.

We are quite optimistic to see that state-of-art instrumentation has now been applied in ocean science to study interactions of TEs and organic matter in seawater, but there is a continuous demand to develop new instruments and protocols to meet the challenging field of marine organometallic compounds. Future developments should allow online separation, pre-concentration, identification and quantification of ligands. Such a development relies on the innovation of separation methods that can isolate the organic molecules with different hydrophobic and hydrophilic properties, or preferably details of the different functional groups that combine with TEs. The online hybridizing instruments should allow the determination of TEs combined with different organic matter, such as polar and non-polar molecules for their concentration and isotope compositions at concentrations of pico-mole per kilogram in seawater or even below. Such an advance of technology will provide further information, for example, about strong and/or weak conditional stability constants beyond electro-chemistry, for which the composition and/or structure of organic molecules is not yet specified and qualification depends on the analytical windows.

Our challenges for the future development include collaborations between chemical and modeling communities in ocean sciences for a better understanding of interactions between TEs and organic ligands in a changing ocean, and also the techniques of parameterization using differential equations to quantify the dynamic nature of organometallic compounds in different hydrographic conditions and the compilation of observational data to validate model behaviors. In doing so, experimental strategies have to be explored that are aligned with advances of analytical tools, for example, new sensors for in situ measurements to be mounted to research platforms, such as gliders, remotely operated vehicles and floats, as well as the combination of Euler and Lagrangian strategies in observation. Another potential advantage is the isotopic fractionation along with the interactions of TEs and ligands, which can be a powerful method to gain knowledge on the critical mechanisms, rate/time and to specify source versus sink terms in element cycles in the oceanic ecosystem. All of these are prerequisites, to better quantify the regime of TEs in seawater and its role in biogeochemical cycles in a global change scenario.

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